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CONTENTS

STRESS-CORROSION CRACKING OF 18-8 Cr-Ni STAINLESS STEELS IN AMMONIUM SULPHATE VESSELS				
by C. Aravindakshan, Ajit Roy and B. K. Banerjee				85
CHARACTERIZATION OF PHASES FORMED IN ACIDULATED ROCK PHOSPHATE AND THEIR ESTIMATION BY X-RAY DIFFRACTION METHOD				
by S. C. Chatterjee, A. Guha and S. K. Ghosh				92
SOME LABORATORY TESTS TO EVALUATE THE EFFICIENCY OF COMBINATION OF ORTHOPHOSPHATE, CHROMATE AND POLYPHOSPHATE AS CORROSION INHIBITOR IN COOLING TOWER WATERS				
by K. M. Verma, M. P. Gupta and A. K. Roy				98
A PILOT-PLANT STUDY ON BIOLOGICAL TREATMENT OF PHENOL-BEARING WASTES				
by R. R. Prasad and B. K. Dutta				102
ROLE OF COMPLEXANTS IN DECREASING PHOSPHATE RETENTION OF SOILS				
by S. G. Misra and S. K. Ojha				108
SHORT COMMUNICATIONS				
BENEFICIATION OF RAJASTHAN ROCK PHOSPHATE				
by M. K. Bardhan, R. K. Dargar and A. K. Roy				113
SOME STUDIES ON PROTECTIVE COATINGS FOR USE IN FERTILIZER PLANTS				
by H. D. Sarkar and A. K. Roy				115
INDIRECT METHOD OF ESTIMATION OF PHOSPHORUS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY				
by K. C. Singhal, A. C. Banerji and B. K. Banerjee				117
A MAGNETIC FIELD MARKER FOR USE WITH ESR SPECTROMETERS				
by G. P. Gupta and P. K. Ghosh				120
DETERMINATION OF SOME TRACE IMPURITIES IN DRINKING WATER BY ATOMIC ABSORPTION SPECTROPHOTOMETRY				
by R. C. P. Sinha, K. C. Singhal and A. C. Banerji				121
ON CALCIUM AND STRONTIUM HYDROXYAPATITES				
by Vijay Mohan Bhatnagar				123
RESPONSE OF AMAN PADDY AND POTATO TO SOIL AND FOLIAR APPLICATIONS OF VARIOUS NITROGENOUS FERTILIZERS				
by S. P. Dhua and S. Roy				124
TETRAPLOIDY IN POMEGRANATE (<i>Punica granatum</i> L)				
by P. K. Das and S. C. Sur				126
ESTIMATION OF UREA BY POLAROGRAPHIC METHOD				
by R. M. Bhatnagar, B. N. Singh and A. K. Roy				128
IN THE INDIAN CONTEXT				
NUCLEAR DESALINATION OF SEA WATER AND FERTILIZER MANUFACTURE				
by S. R. Alagarsamy, J. S. S. Lakshminarayana and M. V. Bopardikar				130
.. .. .				142
NOTES & NEWS				152
NEWS IN BRIEF				155
STATISTICS				

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TECHNOLOGY

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Stress-Corrosion Cracking of 18-8 Cr—Ni Stainless Steels in Ammonium Sulphate Vessels

By

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The causes for cracking of 18-8 Cr-Ni alloy steels in ammonium sulphate manufacturing vessels have been investigated by x-ray diffraction technique on the material of construction and corrosion products. The cracking has been attributed mainly to the residual stresses which give rise to transformation of austenite grains to ferrite and to the creation of crystallographic defects, like lattice imperfections, disordering and slip planes, in the alloy structure.

Intense cracking has been observed in the 18-8 Cr-Ni stainless steel vessels used for ammonium sulphate manufacture by gypsum process. The various portions of the manufacturing vessels were made of either AISI 316, 316L or 321 types of stainless steel. In the evaporation section, the acidity of evaporator is maintained by 0.2-0.3 g./100 ml. of sulphuric acid and trivalent arsenic in the form of sodium arsenite 0.18-0.25 g./100 ml. is added to inhibit corrosion cracking. But, in spite of this, cracking occurs in the vessels. In the evaporation section, sometimes, cracking has developed just two months after commissioning. Therefore, an attempt has been made to understand the causes of cracking by x-ray diffraction analyses of materials of construction and corrosion products.

Experimental

Samples in the form of cut-pieces were collected from the discarded vessels of various equipments. The description and results of visual examination of these samples are given in Table 1.

From visual examination it was seen that all samples were cracked and some of them, viz. Nos. 4 and 5 from evaporator and downcomer, have become even brittle. Therefore, in order to verify the composition of the materials, a semi-quantitative spectroscopic

TABLE 1—VISUAL EXAMINATION OF STAINLESS STEEL SAMPLES

Description of Samples		Remarks
Sample No.	Location	
1	Feed Tank	Thickness about 2 mm.; developed pits of 1-3 mm. dia. and 1 mm. deep.
2	Feed Line	Thickness about 2 mm.; broad cracks have developed; gave way during cutting.
3	U-bend	Thickness about 2 mm.; several spork-like cracks spread throughout.
4	Evaporator	Thickness 2-3 mm.; long big spork-like cracks; material has become brittle.
5	Downcomer	Thickness 3-4 mm.; severe cracks, material has become brittle.
6	Salt Catcher	Thickness about 3 mm.; short cracks.
7	Slurry Line	Thickness about 2 mm.; circular cracks, some pits had been filled by weldings.

analysis for various elements was done for all the above samples by a Russian-made Steeloscope Cπ—11. The results are given in Table 2 from which it can be seen that all the samples are of the type AISI 321 stainless steel.

TABLE 2—SPECTROSCOPIC ANALYSIS OF 18-8 Cr-Ni ALLOY STEEL SAMPLES

Sample No.	Sample From	Elements estimated (other than iron) in percentage				
		Cr	Ni	Mn	Mo	Ti
1.	Feed tank	18-20	8-10	0.9	0.15	0.7
2.	Feed line	18-20	8-10	0.9	0.15-0.30	0.8
3.	U-bend	18-20	8-10	0.9	0.35-0.60	0.7
4.	Evaporator	18-20	8-10	1.0	0.15	0.5
5.	Downcomer	18-20	8-10	0.9	0.15	0.6
6.	Slurry line	18-20	8-10	0.9	0.35-0.60	0.8

X-ray Analysis: Having ascertained the type of alloy steel of the samples, an x-ray diffraction analysis was extended for the identification of crystalline phases in

them. For this purpose specimens were prepared by mild filing of the steel samples at places far away from welded areas. These filings, filled in thin glass capillaries of almost same thickness, were used to obtain the diffraction patterns in Debye-Scherrer cameras of 11.46 and 5.73 cm. diameters with filtered iron radiation at 30 KV. and 10 mA. Specimen from corrosion product was prepared by smooth filing of an area where the product was stuck inside a widely cracked region and filling this powder in a thin glass capillary tube.

A qualitative identification of crystalline phases in the filings revealed that these were of only two prominent phases, viz. body-centred cubic-ferrite and face-centred cubic-austenite, of iron. But the corrosion products showed small amounts of iron- and chromium-ammonium sulphates and oxides of iron along with the above iron phases (Table 3).

TABLE 3—X-RAY DATA FOR 18-8 Cr-Ni ALLOY SAMPLES AND THEIR CORROSION PRODUCTS

Sample No. 1 ^a		γ -Fe, ASTM, 5-0717		α -Fe, ASTM, 6-0696		Corrosion product		γ -Fe ₃ O ₄		β -Fe ₂ O ₃ .H ₂ O ^b		NH ₄ Fe(SO ₄) ₂ ASTM 3-0035		NH ₄ Cr(SO ₄) ₂ ASTM 3-0032	
d (Å)	Int.	d (Å)	Int.	d (Å)	Int.	d (Å)	Int.	d (Å)	Int.	d (Å)	Int.	d (Å)	Int.	d (Å)	Int.
						4.46	vvw	4.85	10						
						3.68	vvw					3.74	40	3.71	75
						3.33	w			3.32	100				
						2.97	vw	2.97	20					2.94	30
						2.65	vvw			2.62	30				
						2.55	w	2.532	100	2.54	70				
						2.43	vw	2.425	8			2.41	50		
						2.27	vvw			2.28	30			2.39	25
						2.100	vvw	2.100	20	2.095	20				
2.083	s	2.08	100			2.080	s							2.07	8
2.032	ms			2.027	100	2.032	s								
										1.945	20			1.86	10
1.803	ms	1.80	80			1.803	ms			1.745	10				
								1.714	15	1.720	5				
						1.695	vvw								
						1.623	vvw	1.617	25	1.635	30				
						1.564	vw					1.56	10	1.57	8
						1.529	vvw			1.515	15				
1.446	vw			1.433	19	1.482	vw	1.485	35	1.485	10				
						1.442	w			1.440	10				
						1.389	vvw			1.375	10	1.39	13		
1.273	m	1.27	50			1.338	w	1.327	6	1.310	5				
						1.272	ms	1.280	10						
								1.266	3						
1.177	mw			1.170	30	1.176	m	1.212	4						
								1.122	4						
1.086	ms	1.083	80			1.085	s	1.093	15						
1.039	mw	1.037	50			1.039	s	1.050	4						
				1.013	9	1.018	ms								

s-Strong, ms-Medium strong, m-medium, mw-medium weak, w-weak, vw-very weak and vvw-very very weak.

a, X-ray data of bulk material of other samples are identical to those of sample No. 1 except in intensity.

b, These values are from *X-ray Identification and Crystal Structures of Clay Minerals*, Editor G. Brown, (Jarrold & Sons Ltd., Norwich, U.K.), 1961, 386.

c, The X-ray powder data was obtained by a 5.73 dia. camera. No values above 5 Å of standard substance quoted above are given.

The alloy steel 18-8 Cr-Ni types are normally supposed to be austenitic and as such they have only one bulk crystalline phase of f.c.c. Fe type. But our analyses of the specimens showed the presence of b.c.c. phase of iron also. Therefore, in order to verify whether ferrite transformation took place as a result of mild filing or not, two sample pieces tested by a magnet, one showing slightly ferro-magnetic (sample 4) and another showing non-ferromagnetic (sample 7) properties as such, were used to obtain the back reflection region in a powder camera of 11.46 cm. Filings obtained by using a non-ferromagnetic filing rod from the same two samples were also used to obtain a full diffraction powder pattern in a 5.73 cm. dia. camera. Then it was found that the non-ferromagnetic sample showed no trace of the ferrite phase and yet filings from both showed the presence of ferrite phase although its overall contents differ much as is evident from their x-ray patterns (Fig. 1). Therefore, an attempt was made to estimate quantitatively the amount of ferrite in each of the sample filings.

Estimation of Phases: It is well known that 'I', the integrated intensity per unit length of the x-ray diffraction line after passing through a specimen of thickness

't' in Debye-Scherrer arrangement, is

$$I = I_0 \frac{e^4 \lambda^3}{m^2 c^4} \frac{V}{v^2} \left[|F_{hkl}|^2 p \cdot \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) \right] e^{-2M} e^{-2\mu t} \quad \dots (1)$$

Where I_0 = intensity of incident beam, e , m = charge and mass of electron, c = velocity of light, λ = wave length of the incident radiation, V = effective volume of the specimen, v = volume of unit cell, F_{hkl} = structure factor of the diffraction line hkl , p = multiplicity factor, e^{-2M} = temperature factor and $e^{-2\mu t}$ = absorption factor, the last two being direct functions of Bragg angle ' θ '.

In the cases of the ferrite and austenite phases of iron, most intense diffraction lines are their 110 and 111 reflections respectively. The Bragg angles as calculated, assuming the unit cell parameters for the phases given by Barrent¹ are very near, viz. ' θ ', are 28.55° and 28.02° for reflections 110 of α -Fe and 111 of γ -Fe respectively. Therefore, if we base our estimation in these two component crystalline specimens of almost same thickness by measuring the integrated intensity of 110 and 111 reflections respectively of them, the last three terms in the equation (1) involving ' θ ' are almost equal. Now, for ferrite and austenite phases two similar equations

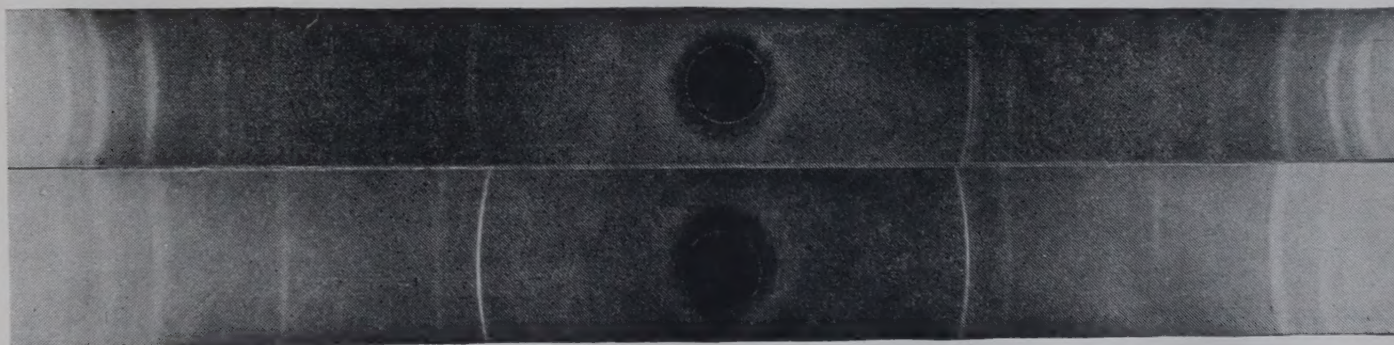


Fig. 1(a)—X-ray diffraction photographs of filings obtained by a 5.73 cm. dia camera of (I) sample No. 4 and (II) sample No. 7.

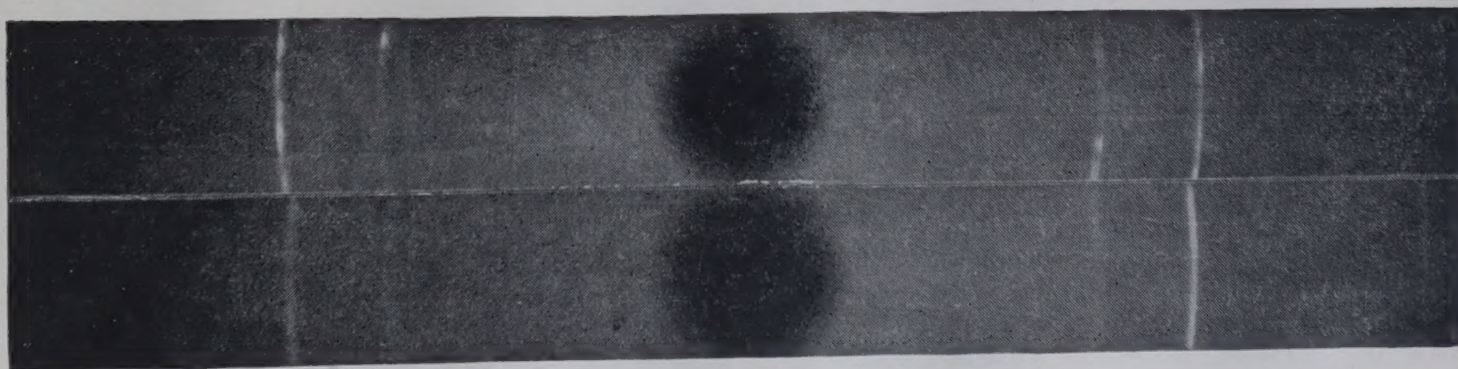


Fig. 1(b)—Back reflection X-ray photographs of bulk material as such, obtained by a 11.46 cm. dia camera of (I) sample No. 4 and (II) sample No. 7.

as equation (1) with subscript 'f' and 'a' are obtained and dividing one by the other, we get,

$$\frac{I_f}{I_a} = \frac{V_f}{V_a} \cdot \frac{v_f}{v_a} \cdot \left[\frac{|F_f| \cdot p_f}{|F_a| \cdot p_a} \right] \quad \dots (2)$$

where $|F_f|$ is the $|F_{110}|$ of the ferrite phase and $|F_a|$ is the $|F_{111}|$ of the austenite phase, or rewriting the equation (2) as the ratio of the volume fractions of the phases, we get,

$$\frac{V_f}{V_a} = \frac{I_f}{I_a} \cdot \frac{v_f}{v_a} \cdot \left[\frac{|F_a| \cdot p_a}{|F_f| \cdot p_f} \right] \quad \dots (3)$$

If there are only two phases in the specimen we get another relation

$$V_f + V_a = 1 \quad \dots (4)$$

Therefore, if there are only two crystalline phases in a specimen, the volume fraction of each component can be estimated if the integrated intensity of certain reflections are measured, as the other terms in the equation (3) can be calculated when their structures are known.

In the present case, for the estimation of ferrite phase in the 18-8 Cr-Ni alloy steel samples, the 011 reflection of ferrite phase and 111 reflection of austenite phase obtained in the same x-ray film were microphotometered (Fig. 2) by a Russian Microphotometer $M\Phi - 4$. The integrated intensities were obtained by calculating the area covered by each peak of each specimen. For better accuracy, both sides of the x-ray films were used. The average value of ratios of integrated intensities of lines were taken to calculate the amounts of ferrite phase in each case of the sample by making use of the relations in equations (3) and (4) and the results are given in Table 5. In the estimation of ferrite in the ferrite-austenite mixture, presence of any carbide was not considered as its percentage was almost negligible and hardly any diffraction line was given by it when filings were analysed.

In the above estimation of phase, the factor F_{hkl} coming in the equation (1) and the corresponding factors in equation (3) involve the atomic scattering powers of various atoms in the unit cell of each phase. If there is any solid solution formation which is usually found to be the case with alloy steels, the intensities, I_f and I_a , may differ from the intensities for those of pure ferrite and austenite phases due to slight differences in atomic scattering powers of chromium and nickel atoms from those of iron atoms for the same Bragg angle ' θ ' (for example, the atomic scattering powers at 0° Bragg angle are for Cr 24, Fe 26 and Ni 28). Therefore, to verify whether there was any appreciable differ-

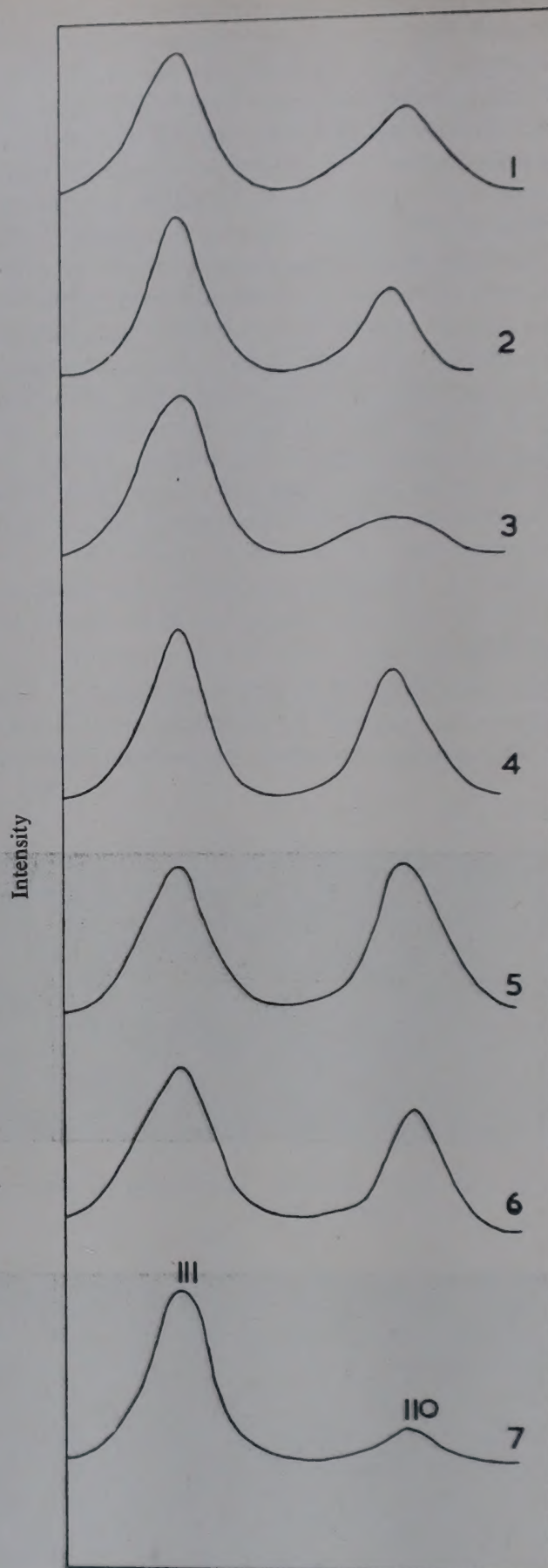


Fig. 2—Microphotometer Trace of 111 Reflection of Austenite and 110 Reflection of Ferrite.

ences between the intensities of reflexion of pure and solid solutions of ferrite and austenite phases of iron, intensity calculations for hypothetical solid solutions with chromium atoms as large as 50 per cent in ferrite phase and with nickel atoms as large as 25 per cent in austenite phase were done. These were more than double the number of all non-ferrous atoms that could have completely gone into solid solutions in 18-8 Cr-Ni alloys. These calculated intensities for pure and solid solutions were then compared with the corresponding observed intensities in the case of sample No. 6 and

found that the discrepancy factors $\frac{\sum |F_o - F_c|}{\sum |F_o|}$, the

ratio of the sum of differences between the observed and calculated structure factors to that of the sum of the observed ones, did not change practically (Table 4). Therefore, solid solutions, if any, which has formed in ferrite and austenite phases, do not introduce any appreciable change in intensity values and any error in the volume estimation of phases due to this is only negligible.

TABLE 4—COMPARISON OF OBSERVED AND CALCULATED F_{hkl} FOR PURE Fe AND SOLID SOLUTION

For Ferrite Phase					
Sl. No.	hkl	F _o	F _{c₁}	F _{c₂}	
1.	110	36.6	35.0	33.7	$\Sigma \left \frac{F_o - F_{c_1}}{F_o} \right = 8.0\%$
2.	200	30.4	28.8	27.8	
3.	211	25.1	25.6	24.8	$\Sigma \left \frac{F_o - F_{c_2}}{F_o} \right = 8.1\%$
4.	220	18.4	23.5	22.6	

For Austenite Phase					
		F _o	F _{c₁}	F _{c₃}	
1.	111	16.8	16.5	16.0	$\Sigma \left \frac{F_o - F_{c_1}}{F_o} \right = 8.0\%$
2.	200	10.7	11.1	16.9	
3.	220	11.5	9.8	9.5	$\Sigma \left \frac{F_o - F_{c_3}}{F_o} \right = 8.7\%$
4.	311	14.9	14.4	15.0	
5.	222	7.1	9.1	9.3	

F_o = Observed Structure Factor

F_{c1} = Calculated structure factor for pure ferrite and austenite

F_{c2} = Calculated structure factor for Fe 50 atom. %, and Cr 50 atom. % solid solution in ferrite phase.

F_{c3} = Calculated structure factor for Fe 75 atom %, and Ni 25 atom. % solid solution in austenite phase.

It might be pointed out that the photographic method, as adopted above in the estimation of crystalline phases, has some advantages over the direct method of estima-

tion by making a standard curve of volume fractions against integrated intensities of a certain reflection from specimens whose components are quantitatively known and then making use of this standard curve for the estimation of a particular phase in an unknown sample or by the internal standard method.²¹ They are: (i) the method can be adopted for estimation of variable quantities of more than two crystalline phases by forming more simultaneous equations and solving them together, and (ii) the experimental errors that are likely to be introduced in the estimation of integrated intensities of reflections by variation in camera diameter, specimen thickness, exposure time, film processing and shrinkage are eliminated as the diffraction lines of all phases are taken only from the same film.

Discussion and Conclusions

Normally all 18-8 Cr-Ni alloy steels are found to be austenitic. But the x-ray analysis of the filings from bulk materials of different sections of the ammonium sulphate plant showed the presence of different amounts of ferrite phase, quantitatively estimated (Table 5). Though none of the bulk material samples, except sample 4, showed practically any presence of ferrite phase, tested by an ordinary magnet, yet the fact that filings from all the samples revealed appreciable amounts of ferrite phase (Table 5) shows that some of the austenite grains have transformed to ferrite structure. This transformation could have taken place by the application of cold working during mild filing. It may be a mechanism as proposed by Nishiyama² Kurdjumow and Sachs³, and Jawson and Wheelor⁴ through successive shearing, extension and contraction forces which allow minor dimensional readjustments for the parameter changes for the transformation. It should be emphasised that the relative movements of atoms for this transformation are very small, the plane of reticular density in austenite, (111) being retained as the closest packed planes, (011)

TABLE 5—X-RAY ESTIMATION OF FERRITE PHASE IN 18-8 Cr-Ni ALLOY STEEL SAMPLES

Sample No.	Sample From	$\frac{I_f}{I_a}$	V_f in %
1.	Feed Tank	0.74	31
2.	Feed Line	0.51	24
3.	U-Bend	0.24	11
4.	Evaporator	0.67	29
5.	Downcomer	1.13	41
6.	Saltcatcher	0.59	27
7.	Slurry Line	0.10	6

in the transformed structure of ferrite. The amount of ferrite transformed would, then, depend upon the direction, type, strength and duration of stresses acting on individual grains during filing. Of course, in the present investigation the amount of ferrite transformed could not be correlated with the filing stresses which is complex in nature.

Thus, a slight amount of applied stress can transform some of the austenite lattices of this AISI 321 type steel into ferrite lattices. In the fabricated equipments certain amounts of stresses are left at the welded joints. These residual stresses along with stresses applied during bending and other fabrication procedure which might remain unrelieved give rise to plastic deformation and transformation of some of the austenite grains to ferrite structure. In fact, all the samples investigated showed traces of ferromagnetism under a strong electromagnetic field of strength above 5000 gauss.

The cold working of a metal, like iron, causes an increase in its rate of corrosion in an acidic medium. This is due to the fact that cold working causes dislocation arrays which will scatter the conductivity electrons and thereby change the electrical properties. There will be difference in solution potential between the cold worked grains and the unaffected grains. Hoar and West⁵ showed that anodic polarization is less for an 18-8 wire under stress than for an unstressed one, which indicates that there is greater ease of metal dissolution when the lattice undergoes plastic deformation. But Uhlig⁶ calculated the change in electromotive force for a severely cold worked metal with a high stored heat absorbed value and found it to be negligible. He concluded that any change in potential was far too small to account for the observed increase in the corrosion rate. This fact then led him to the proposal that the increased corrosion rate was probably caused by precipitation of a second phase during cold working. For a steel the strain-induced precipitate was thought to be iron-nitride and for 18-8 Cr-Ni steel a transformation decomposition product of austenite. Edeleanu⁷ also suggested along the same lines that failures of 18-8 steels occur at temperatures above those at which lattice transformation can occur. But Copson⁸, and Hoar and West⁵ found that pure nickel and pure iron did not show any increase in corrosion rate after undergoing strain unlike for 18-8 stainless steels. Then, it leads to the conclusion that increased corrosion rate in cold-worked alloys may be due to composition gradients created within the alloy slip planes producing dislocations, lattice defects and transformations like austenite to ferrite. These processes increase the rates of diffusion

of interstitial elements and segregation of solute-atoms along dislocations and also at phase domain boundaries. This was further confirmed by Swann⁹, Douglass et al¹⁰ and Troman and Nutting¹¹, who found that in pure metals and alloys where easy cross-slip and dislocation tangling occurred, there was no transgranular susceptibility and that alloys undergoing stress-corrosion cracking had a continuous plane of disordered material which was created by the motion of dislocations through a matrix of short-range order due to their low stacking fault-energy. Components of solid-solution alloy may concentrate preferentially at such lattice imperfections, which then may become anodic or cathodic sites depending upon the electrochemical properties of preferentially concentrated atoms at such sites. Then the lattice site would corrode in the same way as intergranular iron nitrides and carbides accelerate corrosion by their cathodic reaction.

The recent studies on the effect of cold work on stress-corrosion cracking of austenitic alloys by Greenley¹² et al and Burkart¹³ et al have revealed that cold work has deleterious effect on stress-corrosion susceptibility. The time of fracture decreased with increasing amount of cold work and the susceptibility was maximum for a 10 per cent cold worked specimen. The longer time to failure of a more heavily cold worked material was explained by transformation of austenite to quasi-martensite. The short time to failure recorded for a 10 per cent cold worked material was attributed to the fact that this amount of work introduces a near-maximum amount of localized residual stresses into the austenite matrix of the material with a minimum amount of phase transformation occurring. Therefore, the specimens, investigated in the present study, showed a tendency of phase transformation from austenite to ferrite, which in fact is less stress-corrosion resistant compared to martensite and has a definite deleterious effect on its stress-corrosion susceptibility.

It was believed that stainless steel alloys when cathodically polarized in dilute sulphuric acid, do not absorb hydrogen; the hydrogen produced escapes as a gas. But Matsushima¹⁴ et al found that pure ferritic 18-8 Cr-Ni steels fail by hydrogen cracking when they are cathodically polarized in 5 per cent sulphuric acid solution saturated with arsenic trioxide. Whiteman and Troiano¹⁵ showed that temperature and strain-rate dependence of hydrogen-embrittlement of austenitic AISI 310 type stainless steel was almost analogous to that of body-centered cubic iron alloys when it was cathodically polarized in a solution of 1N sulphuric acid with 0.025 g./100 ml. of arsenic trioxide dissolved

in it. Shievely¹⁶ et al observed that at 21°C hydrogen enters and penetrates thin austenitic AISI 310 type stainless steel in sulphuric acid solution under applied cathodic current. Thus, both ferritic and austenitic alloys fail by hydrogen-stress cracking when they are cathodically polarized in dilute sulphuric acid containing arsenic trioxide, but with a difference that in the case of austenitic alloys hydrogen enters the alloy all over the surface and it concentrates to the critical concentrations required for cracking only at accidental notches or other stress raisers on the surface. Recently, Roy and Verma¹⁷ showed that corrosion rate of AISI 321 type stainless steel is quite high in a boiling solution of 0.3 g./100 ml. of sulphuric acid the corresponding potential with respect to calomel electrode being 460 mv towards the cathodic direction. They observed that addition of trivalent arsenic to the solution shifted the potential to the passive direction and the corrosion rate was considerably reduced. The shift was to the extent of 238 mv in the noble direction by an addition of 0.2 g./100 ml. of arsenic trioxide even in presence of 0.2 g./100 ml. of sodium chloride. Therefore, if the concentration of trivalent arsenic becomes low in the acidified ammonium sulphate liquor, hydrogen cracking of the vessels may also occur due to the cathodic polarization of the local action cells.

Again, the 18-8 Cr-Ni stainless steel undergoing stress-corrosion in the ammonium sulphate manufacturing vessels produces the corrosion products of iron-oxides, iron ammonium sulphate and chromium-ammonium sulphate which were revealed by the x-ray diffraction analyses (Table 3). These products produced in the micro-crevices by local electro-chemical actions exert further stresses by their increase in volume—e.g. the volume of Fe_3O_4 is approximately 1.4 times that of steel from which it is formed¹⁸—and acting like wedges at the tip of the crack they open it further as demonstrated by Nielsen¹⁹ and others²⁰. This is in line with our observation that the cracked surfaces are found to be heavily stained by the brown and dark colorations of iron oxides. This way of crack propagation continues until it meets with dislocation tanglings and cross slips which are usually formed in solid solution alloys by its shortrange ordering, or by the spontaneous cracking which makes the region plastically deformed allowing the stresses caused by the wedge action of corrosion products to relax at the tip of the crack. Thus, the stress-corrosion cracking propagates by the combined action of electro-chemical and mechanical mechanisms or by one acting after the other.

To summarize, the following conclusions are derived from the present investigation: (1) The titanium stabilized 18-8 Cr-Ni stainless steels used in the ammonium sulphate manufacturing vessels are not stable with respect to its austenitic structure; (2) the residual stresses in the vessels can cause cold working and plastic deformation, and the grains under stress undergo phase transformation to ferrite structure; (3) plastic deformation and phase transformation create composition gradients and crystallographic defects in the alloy crystal structure; (4) concentration of composition gradients within the alloy set up at imperfection sites, coplanar dislocation arrays, slip planes and antiphase boundaries are the sites for the local electro-chemical effects and subsequent stress-corrosion cracking; and (5) crack propagation is assisted by the wedge action of the corrosion products at the tip of the crack.

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Characterization of Phases Formed in Acidulated Rock Phosphate and Their Estimation by X-Ray Diffraction Method

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In this paper an attempt has been made to identify the various phases present in the rock phosphate, which is treated with different concentration of sulphuric acid, and to develop a method for the estimation of the major components formed. It has been shown that tri-, di- and monocalcium phosphate in the acidulated rock phosphate can be estimated directly when the other components present do not interfere.

Rock phosphate, when treated with various amounts of sulphuric acid, forms different amounts of water-soluble, citrate-soluble and citrate-insoluble materials. According to Wazer¹, the water-soluble phosphates are mostly monocalcium phosphate and citrate-solubles are mostly dicalcium phosphate and monocalcium phosphates.

Acidulated rock phosphates are used as a source of phosphorus to the plants. In an earlier communication², it has been shown that as the acidulation increases, there is an increase in the uptake and yield in the case of maize crop.

The different phases formed during the acidulation of rock and their quantities have a definite role in the P_2O_5 availability to the plants. The conventional chemical methods yield very little information on the crystalline form, state of aggregation and identification of the phases present in various concentration of sulphuric acid-treated rock phosphate. Thus, it is necessary to

develop a method for the estimation of the same by x-ray diffraction method.

Experimental

Materials Used: A sample of Jordan rock phosphate was collected from the Superphosphate Factory, Sindri. Its chemical composition is given in Table 1.

TABLE 1—CHEMICAL ANALYSIS OF JORDAN ROCK PHOSPHATE

Constituents	Percentage
CaO	52.40
P_2O_5	34.45
F_2	5.68
CO_2	4.75
SO_3	Trace
SiO_2	2.5
R_2O_3	0.22
MgO	Nil

Method: The method of acidulation was the same as described in the earlier communication². The chemical analysis of the differently acidulated samples are given in Table 2.

X-ray Diffraction Analysis: All the samples were studied by the Philips X-ray diffractometer PW 1050/51 using nickel filtered CuK α radiation and Geiger counter as a detector. The x-ray tube was kept at 40 KV and

TABLE 2—CHEMICAL ANALYSIS OF ACIDULATED ROCK PHOSPHATE

Acidulation, %	Citrate-soluble P ₂ O ₅ , %	Total Available (Citrate-soluble + water-soluble), P ₂ O ₅ , %	Total Water Soluble P ₂ O ₅ , %	Total P ₂ O ₅ , %	Percentage of Tri- Di- and Monocalcium Phosphate		
					Citrate-insoluble P ₂ O ₅ as Ca ₃ (PO ₄) ₂	Citrate-soluble P ₂ O ₅ as CaHPO ₄ ·2H ₂ O	Water-soluble P ₂ O ₅ as Ca(H ₂ PO ₄) ₂ ·H ₂ O
0 i.e. Rock Phos- phate (untreated)	2.99	2.99	Nil	34	68.22	7.18	0
5	3.6	3.5	Trace	—	65.88	8.4	undetermined
10	4.55	4.60	0.05	30	55.88	10.9	0.09
25	4.83	6.37	1.54	29	52.05	11.59	2.772
50	6.65	12.88	6.23	21.2	18.30	15.96	11.21
75	2.99	16.10	13.11	19.2	6.82	7.18	23.59
100	0	15.9	15.9	15.9	0	0	28.62

TABLE 3—X-RAY DIFFRACTION DATA FOR ACIDULATED ROCK PHOSPHATE

5% Acidulated Product		10% Acidulated Product		25% Acidulated Product		50% Acidulated Product		75% Acidulated Product		100% Acidulated Product		Jordan Rock Phosphate	
dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I
5.92	vvw	5.99	vvw					5.81	ms	5.83	s		
5.22	vvw	5.29	vvw					4.34	vvw	4.33	w		
		4.28	vvw	4.25	vvw	4.25	vvw	4.25	vvw	4.24	vvw		
		4.05	vvw	4.04	vvw								
		3.85	vvw	3.82	vw	3.79	vvw						
3.48	vvw	3.50	ms	3.49	m	3.53	vw	3.64	w	3.64	w	3.48	m
		3.45	w	3.44	w	3.43	w (b)	3.46	ms	3.45	ms		
3.35	w	3.34	w	3.33	w	3.29	w	3.32	w	3.28	vvw	3.21	w
3.212	m	3.20	vw	3.11	vw	3.18	vvw	3.101	vw				
		3.02	w	3.04	vw	2.96	ms	2.97	s	3.05	vvw	3.07	w
2.875	s	2.88	s	2.87	ms	2.89	m						
2.85	vw	2.84	w	2.83	w	2.83	vw					2.81	s
		2.791	w	2.78	s	2.791	s	2.805	ms	2.802	m	2.71	s
		2.681	m	2.674	m	2.673	vw	2.682	vw	2.764	m		
		2.621	m	2.605	m	2.594	vw			2.67	vw	2.65	m
		2.614	w					2.56	vw	2.54	vvw	2.55	vvw
2.62	w											2.26	m
2.44	vw	2.458	vvw	2.44	vvw								
2.26	vvw	2.271	vw	2.269	vw	2.30	vw	2.326	vw				
1.94	vw	1.928	m	1.92	m	2.12	w	2.252	vw	2.235	vvw		
		1.867	vw	1.87	w	1.86	vvw	2.169	vvw	2.185	w	2.15	m
		1.830	m	1.83	m	1.81	w	2.125	w	2.114	vw	2.01	vw
1.90	vvw	1.742	w	1.73	w			1.844	ms	1.848	m	1.96	m
1.732	w	1.496	vvw	1.483	vvw	1.51	vw	1.748	vw	1.826	m	1.85	s
		1.465	vvw	1.46	vw			1.73	vw	1.734	vw	1.81	w
		1.449	vvw	1.443	vw	1.446	vw	1.69	w	1.68	vw	1.75	w
								1.646	vw	1.65	vvw	1.62	vw
												1.55	vw
										1.635	w	1.49	w
												1.44	vw

Note: s—strong, ms—medium strong, m—medium, w—weak, vw—very weak, vvw—very very weak, b—broad

20 mA. The diffraction angles were obtained from the chart recorder at a scanning speed 1°/min. with time constant 2 secs. A standard silicon supplied by Philips was also studied in order to correct the observed 'd' values, if any.

The complete set of samples examined with diffractometer was also studied by the Philips PW 1010 x-ray diffraction unit using nickel filtered $\text{CuK}\alpha$ radiation and 11.46 cm. Philips camera in order to obtain an independent check. The phase identification was done by the usual method of Hanawalt³ et al. The Philips X-ray diffractometer PW 1050/51 was used for the quantitative analysis and the procedure has been described later.

Results

Identification of Phases: The x-ray diffraction data are given in Table 3. The various phases present in different degrees of acidulated rock are summarized in Table 4.

TABLE 4—IDENTIFICATION OF DIFFERENT PHASES PRESENT IN THE ACIDULATED SAMPLES

Acidulation, %	Crystalline Phases		
	Major	Minor	Trace
5	Tri-calcium phosphate	Dicalcium phosphate dihydrate, Gypsum, $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$	Quartz
10	Tri-calcium phosphate	Dicalcium phosphate dihydrate, Gypsum, $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$	Quartz
25	Tri-calcium phosphate	Dicalcium phosphate dihydrate, Gypsum, $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$	Quartz
50	Tri-calcium phosphate and Dicalcium phosphate dihydrate	Mono-calcium phosphate monohydrate, Gypsum, $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$	Quartz
75	Mono-calcium phosphate monohydrate	Dicalcium phosphate dihydrate, Tri-calcium phosphate, Gypsum, $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$	Quartz
100	Mono-calcium phosphate monohydrate	Gypsum, $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$	Quartz

Estimation of Mono-, Di- and Tricalcium Phosphates Method: The method of quantitative analysis by x-ray diffraction can be classified broadly into two groups, viz. (1) direct analysis and (2) internal standard technique.

Ando and Matsuno⁴ applied the quantitative x-ray diffraction method of analysis to fertilizers using an

internal standard. In the present case, an attempt has been made to use direct analysis method to determine the mono-, di- and tricalcium phosphate contents in acidulated rock phosphate.

Reference Compounds: Reagent grades of mono-, di- and tri-calcium phosphates were used as reference compounds. The impurities were checked by taking their diffraction patterns.

Preparation of Samples: Each reference compound was tested to determine the extent of grinding required according to the method described by Ando⁵ et al.

Counting Procedure: Philips x-ray diffractometer PW 1050/51 with Geiger counter was used for the quantitative analysis. Filtered $\text{CuK}\alpha$ radiation with nickel filter was used. A strip chart was run at a scanning speed 1°/min. with time constant 2 secs. in order to check for interference and to select the locations for background measurement. The intensities of the lines were determined from Geiger counts by setting the Geiger tube position manually at the desired angle. The operating conditions for the diffractometer were as follows: x-ray tube 40KV, 20 mA, detector Geiger-Muller counter tube, 1650 V; Multiplication 1; Scale factor 64; time constant 2 secs; scatter slit 1°; scanning speed 1°/min; and paper speed 200 mm./hr. The samples (about 250 mg.) were packed into a holder with a rectangular chamber 10 mm. by 20 mm. and 1 mm. deep.

The intensity of the 3.63 Å ($2\theta=24.61$) for mono-calcium phosphate, 2.791 Å ($2\theta=32.08$) for dicalcium phosphate and 2.89 Å ($2\theta=30.84$) for tricalcium phosphate maximum was used as reference line for intensity measurements. The heights of the selected peak of the reference compounds were determined directly from the counts. The counts were corrected for corresponding background value.

Calibration Curve: Eight samples containing tricalcium phosphate, dicalcium phosphate dihydrate and mono-calcium phosphate monohydrate in the proportion (95, 5, 0), (85, 10, 5), (70, 20, 10), (60, 20, 20), (50, 20, 30), (30, 30, 40), (10, 40, 50) and (0, 50, 50) respectively were prepared as weight per cent basis under identical conditions. 200 mg. of each of the mixture were grounded in an agate mortar for 10 minutes and the peak heights were measured. A calibration curve was drawn by plotting peak heights against concentration of the reference compounds as weight per cent of the sample. The calibration curve is shown in Fig. 1.

Analysis of Acidulated Rock Phosphate: The sample of rock-phosphate treated with various concentration of sulphuric acid was grounded for 10 minutes in an

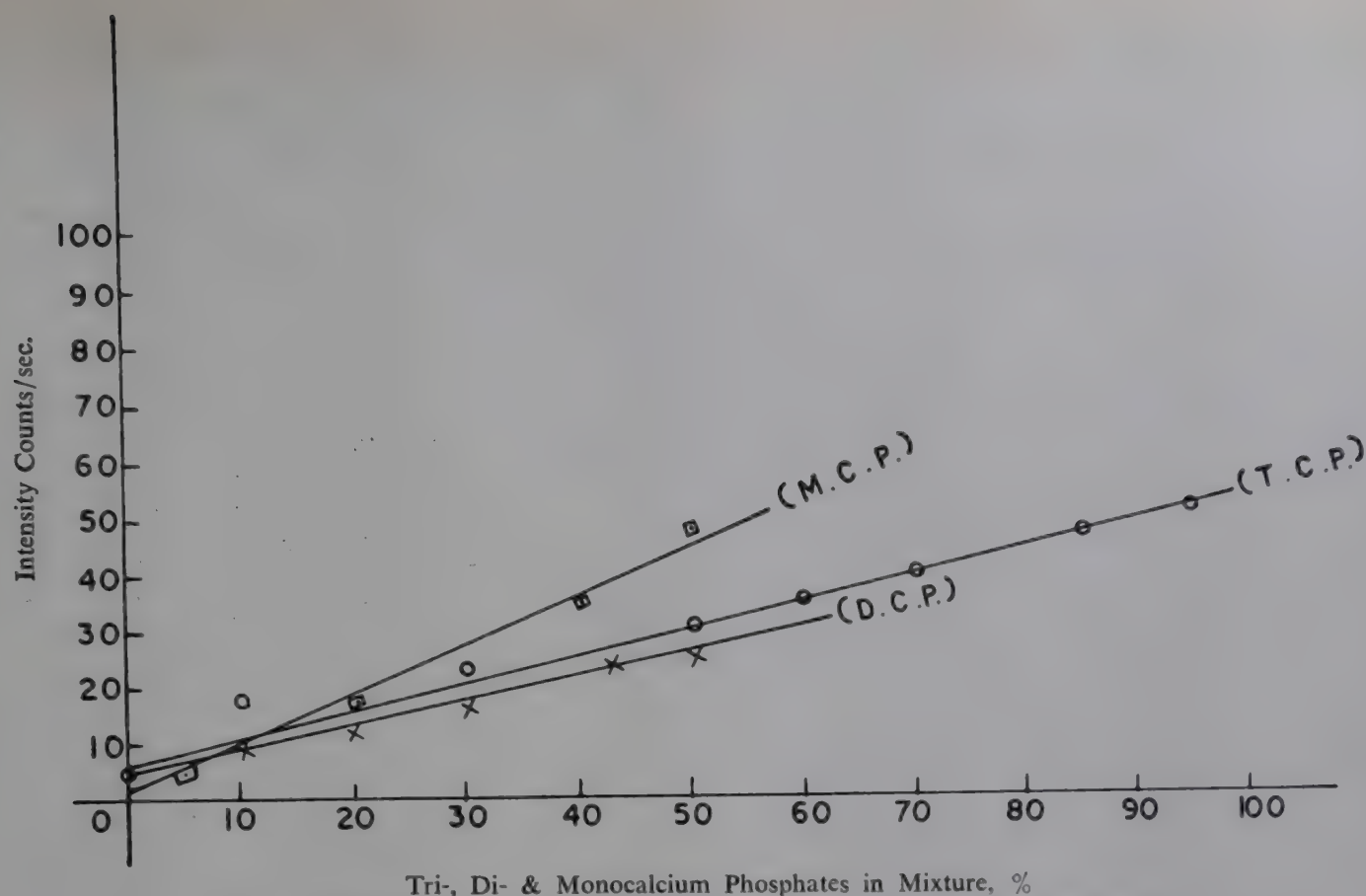


Fig. 1—Working Curve for Determining Mono-, Di- and Tricalcium Phosphates in Acidulated Rock Phosphate.

agate mortar, and the intensity measurements were made from the counts at the desired angle for each component as mentioned above. By referring to the calibration curve (Fig. 1) the intensities of each acidulated rock phosphate were then used to determine the percentage of mono-, di- and tri-calcium phosphate in them.

Results

The results are shown in Tables 5 and 6.

Discussion

The peak used for the determination of each component was chosen on the basis of strong intensity, the

TABLE 5—INTENSITY MEASUREMENT AND ESTIMATION OF DIFFERENT MIXTURES PREPARED FROM TRI-, DI- AND MONOCALCIUM PHOSPHATES (ALL VALUES HAVE BEEN CORRECTED FOR BACKGROUND.)

Percentage of Tri-, Di- and Monocalcium Phosphate in the Mixture			No. of Counts/sec.			Percentage of Tri, Di- and Monocalcium Phosphate Calculated from Equation 1			Percentage of Tri-, Di- and Monocalcium Phosphate by Chemical Analysis		
Tri-	Di-	Mono-	Tri-	Di-	Mono-	$\text{Ca}_3(\text{PO}_4)_2$	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	$\text{Ca}_3(\text{PO}_4)_2$	$\text{CaHPO}_4 \cdot \text{H}_2\text{O}$	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$
95	5	0	500	70	20	94.1	4.9	0	95.25	4.75	0
85	10	5	460	90	50	85.9	9.6	4.5	86.45	9.3	4.25
70	20	10	390	120	100	68.8	19.3	9.6	70.22	19.28	10.5
60	20	20	340	120	170	59.2	19.2	19.3	—	—	20.9
50	20	30	300	120	270	48.9	19.3	30.5	49.5	19.3	31.2
30	30	40	220	140	340	30.45	30.45	39.42	29.6	28.3	42.1
10	40	50	170	220	470	9.3	39.45	50.3	9.7	38.3	52.0
0	50	50	60	240	470	0	50.32	50.29	—	—	—

TABLE 6—PERCENTAGE OF Tri-, Di- AND MONOCALCIUM PHOSPHATES IN THE ACIDULATED ROCK PHOSPHATE

Acidulation, %	No. of Counts/sec. (corrected)			Percentages of Tri-, Di- and Monocalcium Phosphates (from the graph, Fig. 1)			Percentages of Tri-, Di- and Monocalcium Phosphate found by Chemical Analysis (Table 2)			Percentages of Tri-, Di- and Monocalcium Phosphate (vide Equation 1)		
	Tri-	Di-	Mono-	Tri-	Di-	Mono	Citrate- insoluble P ₂ O ₅ as Ca ₃ (PO ₄) ₂	Citrate- soluble P ₂ O ₅ as CaHPO ₄ 2H ₂ O	Water- soluble P ₂ O ₅ as Ca(H ₂ PO ₄) ₂ H ₂ O	Ca ₃ (PO ₄) ₂	CaHPO ₄ 2H ₂ O	Ca(H ₂ PO ₄) ₂ H ₂ O
5	375	80	21	66	7.8	0	65.88	8.4	Undetermined	65.94	7.93	0
10	330	86	12	56	9.8	0	55.88	10.9	0.09	54.87	10.65	0.8
25	298	95	31	51.15	11.4	2.1	52.05	11.59	2.772	51.34	11.48	2.34
50	148	105	96	17.9	14.6	10.2	18.30	15.96	11.21	18.45	15.51	10.88
75	83	72	206	6.1	6.8	23.0	6.82	7.18	23.59	6.45	7.19	23.40
100	25	30	240	0	0	27.1	0	0	28.62	0	0	28.22
0 i.e.	390	76	5	69.0	7.4	0	68.22	7.18	0	69.27	7.12	0
Rock Phosphate (untreated)												

reproducibility of its height and non-interference by peaks of other compounds.

The intensity of a peak in x-ray diffraction pattern varies with the absorption characteristics of the sample. In order to test whether the matrix effect due to the difference of mass absorption co-efficients of different components was a significant source of error, Karlak and Burnett's method⁶ was used in the present investigation. Recently they have derived a general equation for the quantitative analysis of mixed crystalline phases. This unifying equation, which is applicable for quantitative analysis by x-ray diffraction without an internal standard, accounts both for absorption effects and contributions from all possible components. Their results are embodied briefly in two mathematical expressions (1) and (2) involving ordinary relative intensity constant characteristics of pairs of substances, quantities determined from the pattern of the unknown and the individual weight fractions. The final equation can be written as

$$x_j = \frac{D_j}{n-1} \quad j=1,2,\dots,n \quad \dots (1)$$

$$D + \sum_{j=1}^{n-1} D_j$$

where D is the determinant of co-efficient of $(a_{ij} - a_{kj} R_{ik}) / C_{jn}$ where i's refer to rows and the j's to columns and D_j is the determinant resulting from the replacement of the jth column of D by the column of constants appearing in the equation.

$$a_{kn} R_{nk} - a_{nn} = C_{1n} (a_{n1} - a_{k1} R_{nk}) x_{1n} + \dots + C_{n-1,n} (a_{n,n-1} - a_{k,n-1} R_{nk}) x_{n-1,n} \dots \dots (2)$$

where x_j is the weight fraction of component j, a_{ij} is the relative intensity.

Now evaluating the determinant x_j 's can be calculated by inserting the appropriate D's in the equation (1) and a sample calculation for 10 per cent only is shown below:

TABLE 7—RELATIVE INTENSITY NOTATION FOR THREE-COMPONENT SYSTEM

j=1	j=2	j=3
1 a_{11}	a_{12}	a_{13}
2=i a_{21}	a_{22}	a_{23}
3 a_{31}	a_{32}	a_{33}

TABLE 8—RELATIVE INTENSITY CONTRIBUTING TO DIFFERENT LINES USED FOR ANALYSING MIXTURE OF Tri-Di- AND MONO-CALCIUM PHOSPHATES

Intensity, i	Bragg angle $2\theta^\circ$	Components j=1 Ca ₃ (PO ₄) ₂	j=2 CaHPO ₄ 2H ₂ O	j=3 Ca(H ₂ PO ₄) ₂ H ₂ O
1	30.84	$a_{11}=0.647$	$a_{12}=0$	$a_{13}=0$
2=k	32.08	$a_{21}=0$	$a_{22}=0.2318$	$a_{23}=0$
3	24.61	$a_{31}=0$	$a_{32}=0$	$a_{33}=0.08$

Since, in this case there is no interference at the angle of measurements of each component by others, a_{kn}

R_{nk} and $C_{jn}=0$ Hence, $D_j = a_{nn}$

so, $D_1 = a_{11} = 0.647$, $D_2 = a_{22} = 0.2318$ and

$D_3 = a_{33} = 0.08$

where 'a's are the ratio of intensity of a particular component in a mixture to that of the pure component.

Now $\sum_{j=1}^{n-1} D_j$ is calculated as follows:

when $j=1$, $D_1 = 0.647 \times 0.2318 \times 0.08 = 0.01199$

$j=2$, $D_2 = 0.2318 \times 0.08 = 0.01854$

$j=3$, $D_3 = 0.08$

Now inserting $\sum_{j=1}^3 D_j$ and D_j values in equation (1)

the weight fraction of each component is obtained as follows:

X_1 (weight fraction of T.C.P.) = 54.87 per cent

X_2 (" D.C.P.) = 10.65 " "

X_3 (" M.C.P.) = 0.8 " "

It can be seen that compositions computed by x-ray analysis are usually lower than those determined by chemical analysis (Table 4). In chemical analysis the

P_2O_5 content is generally computed as citrate insoluble P_2O_5 which was assumed to be as $Ca_3(PO_4)_2$, citrate-soluble P_2O_5 , as $CaHPO_4 \cdot 2H_2O$ and $Ca(H_2PO_4)_2 \cdot H_2O$ and water-soluble P_2O_5 as $Ca(H_2PO_4)_2$, H_2O . Because of these uncertainties in the absolute determination of each phase the chemical analysis shows higher results than x-ray analysis.

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Some Laboratory Tests to Evaluate the Efficiency of Combination of Orthophosphate, Chromate and Polyphosphate as Corrosion Inhibitor in Cooling Tower Waters

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For cooling waters, orthophosphate has been tried as an inhibitor in combination with chromate and polyphosphate. An orthophosphate concentration of 100-150 ppm as PO_4 along with 40 ppm chromate as CrO_4 and 10 ppm polyphosphate as PO_4 was found to be the most suitable combination for corrosion prevention by cooling waters containing high concentration of corrosive ingredients and was found to be much superior to the simple chromate-polyphosphate treatment.

In the reduction of waterside corrosion, inhibitors such as chromates, phosphates, nitrites, alkalis and several others have been used. It has been pointed out that these inhibitors acting anodically are able to provide satisfactory protection provided the concentration level is sufficiently high¹; when the concentration level is insufficient, pitting and tuberculation result. Kahler²⁻⁵ et al, Brandel⁶, and Brooke⁷ et al have all advocated the use of chromate polyphosphate combination as inhibitor of corrosion by cooling waters. Daehen⁸ has advocated the use of orthophosphate in combination with chromate while Palmer⁹ has used orthophosphate in combination with an oxidizing agent, viz. chromate or persulphate, and the results have been encouraging.

Extensive work has been done in this laboratory¹⁰⁻¹⁵ to find out suitable inhibitors for minimizing the corrosion by cooling waters. Typical analysis of the cooling tower water is given in Table 1; at times due to contamination of dust from the salt plants and bacterial action, the cooling waters get highly polluted and the concentration of corrosive ingredients attain high values as, for example, total nitrogen content of 300 ppm, 150 ppm of chloride and 150 ppm of sulphate. Our results¹⁰ have shown that a chromate polyphosphate

combination of 40 ppm CrO_4 and 20 ppm PO_4 is quite effective to reduce the corrosion by cooling waters to a low value but when the concentration of contaminants increase to high values the efficiency of the inhibitor combination is reduced and even an increase in the polyphosphate content to 40 ppm of PO_4 does not produce much improvement.

TABLE 1—TYPICAL ANALYSIS OF COOLING TOWER WATER
(pH=6.2-7.9)

(Only the maximum and minimum values have been given to indicate the range.)

Ingredients	Concentration, ppm
*M as CaCO_3	1-10
Ammoniacal N	0.5-2.3
Nitrite + Nitrate N	5.0-11.0
Cl	0.4-7.6
SO_4	36-79
Ca	50-60.5
Total Dissolved Solids	166-304.5
Total Suspended Solids	10-60

*M—denotes methyl orange alkalinity. None of the samples analysed contained phenol-phthalein alkalinity and phosphate.

In the present work, recourse has been taken to the addition of orthophosphate along with chromate and polyphosphate. The effects of different concentrations of orthophosphate alone and in combination with chromate and polyphosphate on the corrosion rates of mild steel, brass and admiralty were studied under simulated cooling tower conditions in waters containing high concentrations of corrosive ingredients, such as ammoniacal- and nitrate-nitrogen, chloride and sulphate radicals. As an increased quantity of ortho-phosphate causes increased sludge formation, experiments were also done to study the effect of these corrosion inhibitors on sludge formation.

Experimental

Rectangular test coupons of $6.2 \times 1.0 \times 0.2$ cm. size of mild steel, brass and admiralty metal were taken for experiment. Mild steel corresponded to specification 1RSM 16/49 manufactured by Messrs Tata Iron and Steel Co., while admiralty metal analysed as Cu 75.16, Zn 23.08 and Sn 1.1 per cent and brass as Cu 62.24 and Zn 37.32 per cent. The corrosion experiments were done under fully immersed, simulating cooling tower conditions at a temperature of $52 \pm 0.5^\circ\text{C}$ as described in a previous communication¹⁰. For surface preparation, the coupons were finally finished on '0' emery paper and degreased in boiling toluene. Extra quantities of ammonium nitrate, sodium chloride and sodium sulphate were added to the cooling tower waters to increase the amounts of these ingredients when desired. Sodium dichromate, sodium hexametaphosphate and potassium dihydrogen phosphate were added to introduce desired quantities of chromate, polyphosphate and orthophosphate. The pH values were maintained in the range of 7 to 8. The loss in weight was expressed as mg./sq. dm./day.

For sludge formation experiments, requisite amounts of ingredients were dissolved together in the ratio in which they were taken for corrosion experiments, the pH was adjusted and then the mass was kept for 24 hours at $52 \pm 0.1^\circ\text{C}$. At the end of the period, the total sludge formed was estimated¹⁰. All the chemicals used were of BDH analytical reagent grade.

Results and Discussion

Corrosion in Uninhibited Water: The results in Table 2 show that in uninhibited cooling water the corrosion rates of mild steel, brass and admiralty metal were 128.5, 12.5 and 10.6 m-dd respectively. With the increase in the contents of corrosive ingredients the corrosion rates of mild steel, brass and admiralty increased further.

The high values of these ingredients were maintained as at times their concentration in cooling water reaches this range.

Effect of Chromate-Polyphosphate: With the addition of 40 ppm chromate and progressive addition of 10 and 20 ppm polyphosphate along with chromate, the corrosion rates were further reduced and a 40:20 ppm chromate polyphosphate content was able to reduce the corrosion rate to 14.8, 11.9 and 10.7 m-dd respectively. This clearly indicated that although a 40:20 ppm chromate polyphosphate content was able to reduce the corrosion rate, very low values could not be attained when concentration of contaminants was high.

Effect of Chromate-Polyphosphate and Orthophosphate: With 1000 ppm orthophosphate, the corrosion rates of mild steel, brass and admiralty were reduced to very low values of 4.7, 3.3 and 2.2 m-dd respectively and coupons were entirely clear. With the progressive decrease in the orthophosphate content to 50 ppm the inhibitive action gradually decreased and only an orthophosphate content of 500 ppm afforded complete protection to mild steel, brass and admiralty. Below this orthophosphate level, mild steel developed etching and pitting tendencies while brass and admiralty were protected even at lower orthophosphate levels.

With the addition of 40 ppm chromate the inhibitive action of orthophosphate was increased considerably, so much so that even an orthophosphate concentration of 250 ppm together with 40 ppm chromate was able to afford complete protection and the corrosion rates of mild steel, brass and admiralty were of the same order as with 500 ppm orthophosphate alone. There was a marked reduction in pitting and etching tendencies in case of mild steel at lower orthophosphate concentrations.

With the addition of 10 ppm polyphosphate along with 40 ppm chromate the corrosion rates were further reduced. The inhibitive action of 100 ppm orthophosphate along with 40 ppm chromate and 10 ppm polyphosphate was of the same order as with 250 ppm orthophosphate + 40 ppm chromate or 500 ppm orthophosphate alone and much better than the chromate-polyphosphate combination of 40:20 ppm. The main effect of 10 ppm polyphosphate appears to be complete elimination of slight pitting tendencies which were apparent with 100 ppm orthophosphate and 40 ppm chromate. With further increase in polyphosphate concentration to 20 ppm the corrosion rates were reduced slightly at all concentration of orthophosphate but the effect was not very well marked.

TABLE 2—EFFECT OF ORTHOPHOSPHATE, CHROMATE AND POLY-PHOSPHATE ON THE CORROSION RATE OF MILD STEEL, BRASS AND ADMIRALTY IN COOLING TOWER WATER

Vol. of solution-20 l., Rate of circulation-2.6l gals/min., Temperature $52 \pm 0.5^\circ\text{C}$; pH 7.0-8.0; Duration of experiment 24 hours

Exp. No.	Media	Inhibitor Concentration, ppm			Corrosion Rate, mg./sq. dm/day			Remarks
		Ortho-phosphate as PO_4	Dichromate as CrO_4	Poly-phosphate as PO_4	Mild Steel	Brass	Admiralty	
1	2	3	4	5	6	7	8	9
1.	Cooling water				126.5	12.5	10.6	General corrosion
2.	Cooling water containing 150 ppm of ammoniacal nitrogen and 150 ppm of nitrate nitrogen				432.7	87.9	78.9	-do-
3.	-do-	—	40	—	28.2	18.5	13.9	With mild steel pittings occur.
4.	-do-	—	40	10	20.9	13.4	11.6	With mild steel pittings are much reduced than Expt. 3.
5.	-do-	—	40	20	14.8	11.9	10.7	Coupons are clear.
6.	-do-	1000	—	—	4.7	3.3	2.2	-do-
7.	-do-	1000	40	—	4.3	2.8	1.5	-do-
8.	-do-	1000	40	10	3.8	2.0	0.9	-do-
9.	-do-	1000	40	20	2.2	1.2	0.3	-do-
10.	-do-	750	—	—	9.5	4.8	4.4	-do-
11.	-do-	750	40	—	5.3	3.8	2.5	-do-
12.	-do-	750	40	10	4.2	3.1	1.9	-do-
13.	-do-	750	40	20	3.9	1.9	1.0	-do-
14.	-do-	500	—	—	11.4	7.7	6.9	-do-
15.	-do-	500	40	—	6.5	5.0	4.2	-do-
16.	-do-	500	40	10	5.8	4.2	3.8	-do-
17.	-do-	500	40	20	5.1	3.3	2.9	-do-
18.	-do-	250	—	—	13.5	8.8	7.2	Slight etch marks with mild steel
19.	-do-	250	40	—	9.0	6.8	5.6	Coupons are clear.
20.	-do-	250	40	10	7.7	5.9	4.8	Coupons are clear.
21.	-do-	250	40	20	6.3	5.0	3.7	-do-
22.	-do-	150	—	—	13.9	10.0	8.7	Some pits are observed in case of mild steel.
23.	-do-	150	40	—	9.8	7.5	6.0	Some etch marks in case of mild steel
24.	-do-	150	40	10	7.3	7.0	5.1	Coupons are clear.
25.	-do-	150	40	20	6.6	5.5	4.6	-do-
26.	-do-	100	40	—	14.9	10.9	9.5	Some pits are observed in case of mild steel but less in presence of chromate than in its absence.
27.	-do-	100	40	—	10.5	8.8	7.3	Coupons are clear.
28.	-do-	100	40	10	8.6	7.2	4.9	-do-
29.	-do-	100	40	20	7.3	5.9	4.3	-do-
30.	-do-	50	—	—	15.5	12.9	11.8	Pitting is observed in case of mild steel.
31.	-do-	50	40	10	13.5	9.7	8.2	-do-
32.	Cooling water containing 150 ppm of ammoniacal nitrogen, 150 ppm of Cl and 150 ppm of SO_4							
33.	-do-	1000	40	10	4.0	2.4	1.4	Coupons are clear
34.	-do-	1000	40	20	2.9	1.6	0.8	-do-
35.	-do-	750	40	20	4.6	2.9	1.6	-do-
36.	-do-	500	40	10	7.3	5.1	4.3	-do-
37.	-do-	500	40	20	5.9	3.5	3.2	-do-
38.	-do-	250	40	10	8.8	6.4	—	-do-
39.	-do-	250	40	20	7.6	6.0	4.9	-do-
40.	-do-	150	40	10	9.6	7.2	5.4	-do-
		100	40	10	10.0	7.4	5.8	Some etch marks observed in case of mild steel.

With increased corrosivity of cooling water due to additional chloride and sulphate contents, an orthophosphate concentration of 150 ppm with 40 ppm of chromate and 10 ppm of polyphosphate was able to afford complete protection to mild steel, brass and admiralty.

Sludge Formation: Table 3 gives a comparative idea about the sludge formed in presence of different inhibitor concentrations in the laboratory tests. Though the sludge formed in laboratory test may not give an exact idea about the actual happenings in the plant conditions, it definitely gives a comparative idea about the conditions in the plants. It will be observed that the maximum

TABLE 3—EFFECT OF ORTHOPHOSPHATE, CHROMATE AND POLYPHOSPHATE ADDITIONS ON SLUDGE FORMATION IN COOLING TOWER WATER

Media—Cooling tower water containing 150 ppm of ammoniacal N and 150 ppm of nitrate Nitrogen
Temp.— $52 \pm 0.1^\circ\text{C}$; Duration of Test 24 hours

Expt. No.	Conc. of Ortho-phosphate PO_4 , ppm	Conc. of Dichro-mate CrO_4 ppm	Conc. of Poly-phosphate PO_4 , ppm	Sludge Formed, ppm	
				at pH 7.0	at pH 8.0
1.	1000	—	—	121.3	135.3
2.	1000	40	—	124.6	139.5
3.	1000	40	20	99.6	112.0
4.	750	—	—	114.0	128.0
5.	750	40	—	118.5	132.8
6.	750	40	10	100.5	110.5
7.	750	40	20	94.5	102.0
8.	500	—	—	110.3	126.7
9.	500	40	—	117.5	130.7
10.	500	40	10	95.6	100.5
11.	500	40	20	90.5	95.8
12.	250	—	—	96.5	102.5
13.	250	40	—	100.8	108.5
14.	250	40	10	85.5	90.5
15.	250	40	20	80.4	84.9
16.	150	—	—	49.2	52.5
17.	150	40	—	53.0	55.5
18.	150	40	10	36.0	45.5
19.	150	40	20	33.0	40.2
20.	100	—	—	35.0	36.85
21.	100	40	—	37.4	41.2
22.	100	40	10	31.6	35.2
23.	100	40	20	30.0	34.0
24.	50	—	—	26.0	28.8
25.	50	40	—	28.0	30.0
26.	50	40	10	22.2	26.5
27.	50	40	20	21.0	24.0
28.	—	40	10	10.5	12.5
29.	—	40	20	12.0	15.2

sludge was formed at an orthophosphate concentration of 1000 ppm and the quantity decreased with decrease in the concentration of orthophosphate. Chromate appeared to increase slightly the sludge formation while polyphosphate produced an appreciable decrease at the corresponding orthophosphate concentration. The sludge formed at pH 7 was always less than that at pH 8. Both these values were selected for study as the pH of the cooling water varies between these two limits, particularly when a chromate-polyphosphate treatment is applied.

It will be seen (Table 3) that at an inhibitor concentration of 100 ppm orthophosphate +40 ppm chromate +10 ppm polyphosphate, the sludge formed was 31.6 and 35.2 ppm at pH values of 7 and 8 respectively, while for a combination of 150 ppm orthophosphate, 40 ppm chromate and 10 ppm polyphosphate, the respective values were 36.0 and 45.5 ppm at the two pH levels. Water analysis (Table 1) shows that the values of total suspended solids varied in the range of 10 to 60 ppm. It has, however, been observed that under actual plant conditions in the presence of high concentrations of contaminants, the total suspended solids attain a value as high as 160 ppm. Though the sludge formed by 150 ppm of orthophosphate +40 ppm chromate +10 ppm of polyphosphate was definitely higher than that formed by a 40-20 ppm chromate polyphosphate combination, still the sludge formed in the former case was much less than what is naturally formed in the cooling towers even in absence of high concentration of corrosive ingredients.

It may, thus, be concluded that depending on the corrositivity of water, inhibitor combinations of 100 ppm orthophosphate +40 ppm chromate +10 ppm polyphosphate and 150 ppm orthophosphate +40 ppm chromate +10 ppm polyphosphate can be used in cooling towers without the risk of excessive sludge formation. These combinations were more effective than simple chromate polyphosphate combinations.

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A Pilot-Plant Study on Biological Treatment of Phenol-Bearing Wastes

By

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The biological oxidation of phenol by bacterial culture developed in this laboratory from garden soil was studied by continuous bench-scale and pilot plant operations. Phenol upto a concentration of 440 mg./l. was destroyed completely in 6-7 hours with an aeration rate of 3m³/min./m³. at room temperature (29-34°C). The process is suitable for commercial application for the treatment of phenolic wastes.

The biological processes for the destruction of phenols have been investigated in recent years. The development of a special bacterial culture for oxidation of phenols has given rise to the installation of plants for the treatment of phenolic effluents by bacterial oixdation. A large number of soil bacteria, when properly cultivated, was found to decompose phenol¹. The decomposition of phenol in these processes was found to be a biochemical reactions², which depends on temperature, aeration, nutrients, etc. A bacterial culture developed in our laboratory from garden soil was found to decompose phenol quite rapidly³. The rate of aeration, temperature and pH of the medium were found to have an important effect on the rate of phenol oxidation. Laboratory experimental data on the oxidation of phenol by a bacterial culture indicated that a temperature of about 37°C and an air-rate of 3m³/min/m³, the oxidation of phenol was most favourable³.

The results obtained from laboratory experiments conducted by a batch process were verified in continuous systems in small bench-scale and experimental pilot-plant. The description and results of the bench-scale

and pilot-plant studied for oxidation of phenol by bacterial culture from garden soil are described in this paper.

Experimental

(1) BENCH SCALE STUDY

(a) *Description of Bench-Scale Unit:* The unit consists of three one-litre conical flasks with side-connections, arranged in series. The phenolic liquor is fed into the first flask at a uniform rate. The liquid flows from the bottom of the first flask and enters near the top of the second flask and from the bottom of the second flask to near the top of the third flask. From the bottom of the third flask it flows out to a receiving bottle. The nutrient mixture, comprising 0.1 g. each of potassium dihydrogen phosphate, magnesium sulphate, ammonium sulphate, a trace of ferrous sulphate and 0.05 g. of sodium chloride dissolved in 100 ml. of water, is added from a burette into the first flask. Air is passed through the three flasks continuously, the air-rate being measured by means of a wet gas meter. Any sludge collected in

the receiving bottle is recirculated in the first flask. The arrangement of the apparatus is shown in Fig. 1.

(b) *Procedure*: The average flow-rate of phenolic liquor ranged from 0.28 to 0.5 l./hr. and the initial concentration of phenol ranged from 465 to 500 mg./l. The temperatures studied were in two ranges, viz. (a) 29-33°C and (b) 39-40°C. The average air-rate maintained in all the experiments was 3m³/min/m³ in each of the vessels. The phenol concentration was determined by the modified permanganate value method⁴ for routine follow-up. The samples of solutions from each vessel were tested at intervals of two hours (Table 1). At the start of the experiment, i.e. at zero hour, the initial concentration of phenol present already in the system varied from 4 to 300 mg./l. As the liquor travels from the first to the third flask, phenol is oxidized during the detention period, which varied, since the rate of flow of the phenolic liquor varied. In the temperature range 29-33°C (Table 1), it could be observed that in a detention period of 8 hours the phenol has been almost completely destroyed. At higher flow-rate, i.e. lower detention period, the oxidation of phenol is not complete (Table 1, Sl. No. 5). At higher temperature, viz., 39-40°C, phenol oxidation rate is slower and appreciable destruction occurs only at a higher detention period of 10 hours (Table 1, Sl. No. 6-9). It has also been stated that

in these ranges mesophilic organisms predominate though they are generally more efficient at 30°C⁵. It is evident from Table 1 that for a normal temperature around 30°C, 8 hours' detention time is quite adequate for complete oxidation of phenol in concentration upto 500 mg./l.

(2) PILOT-PLANT STUDY

On the basis of the above bench-scale experimental data a pilot-plant was designed and installed (Figs. 2A and 2B). The pilot plant consists of a phenol oxidation tank (A) 6 ft. long, 9 inches wide and 2 ft. 6 inches deep. It is divided into 8 equal compartments, each 9 inches long, by means of baffle plates (B) each rising from the bottom upto 6 inches from the top. The first, third, fifth and seventh baffles have a number of circular openings near the top. The second, fourth and sixth baffles have semi-circular openings at the bottom. The last compartment is fitted with a cylindrical tube (C) of three inches diameter rising from the bottom upto 6 inches from the top. It has an outlet tube (D) of one inch diameter fitted one inch from the top. The last compartment is also provided with a drain (E) of 1/2 inch diameter fitted with a valve. Air is supplied by a 2 inches header (F) running above the oxidation tank. Air connections to each of the compartments except

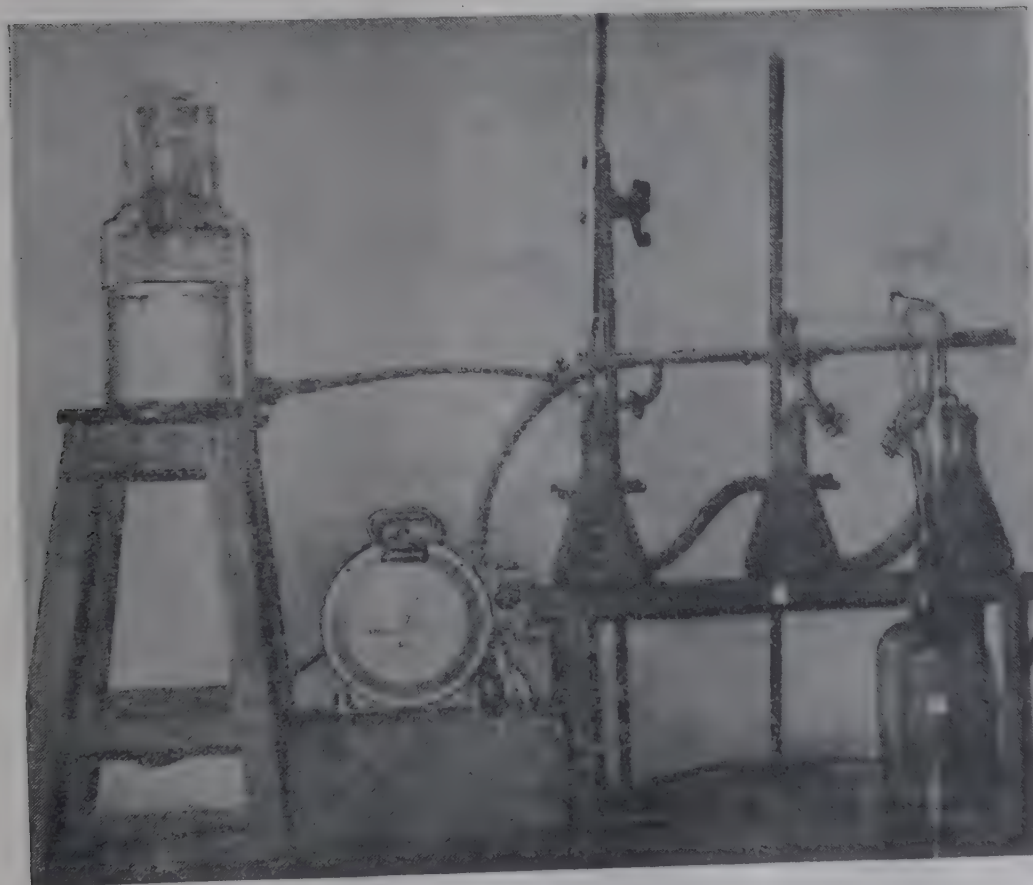


Fig. 1—Biological Oxidation of Phenol (Bench-Scale).

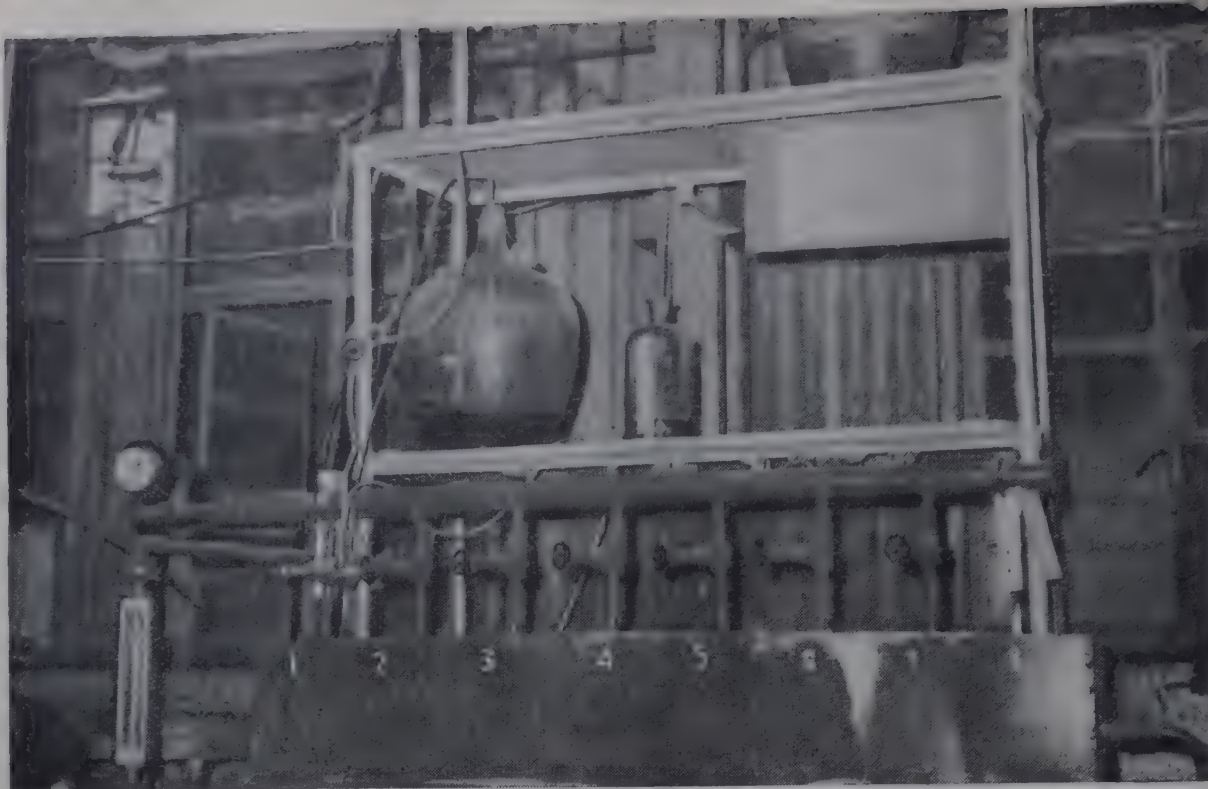


Fig. 2A—Biological Oxidation of Phenol.
(Pilot Plant)

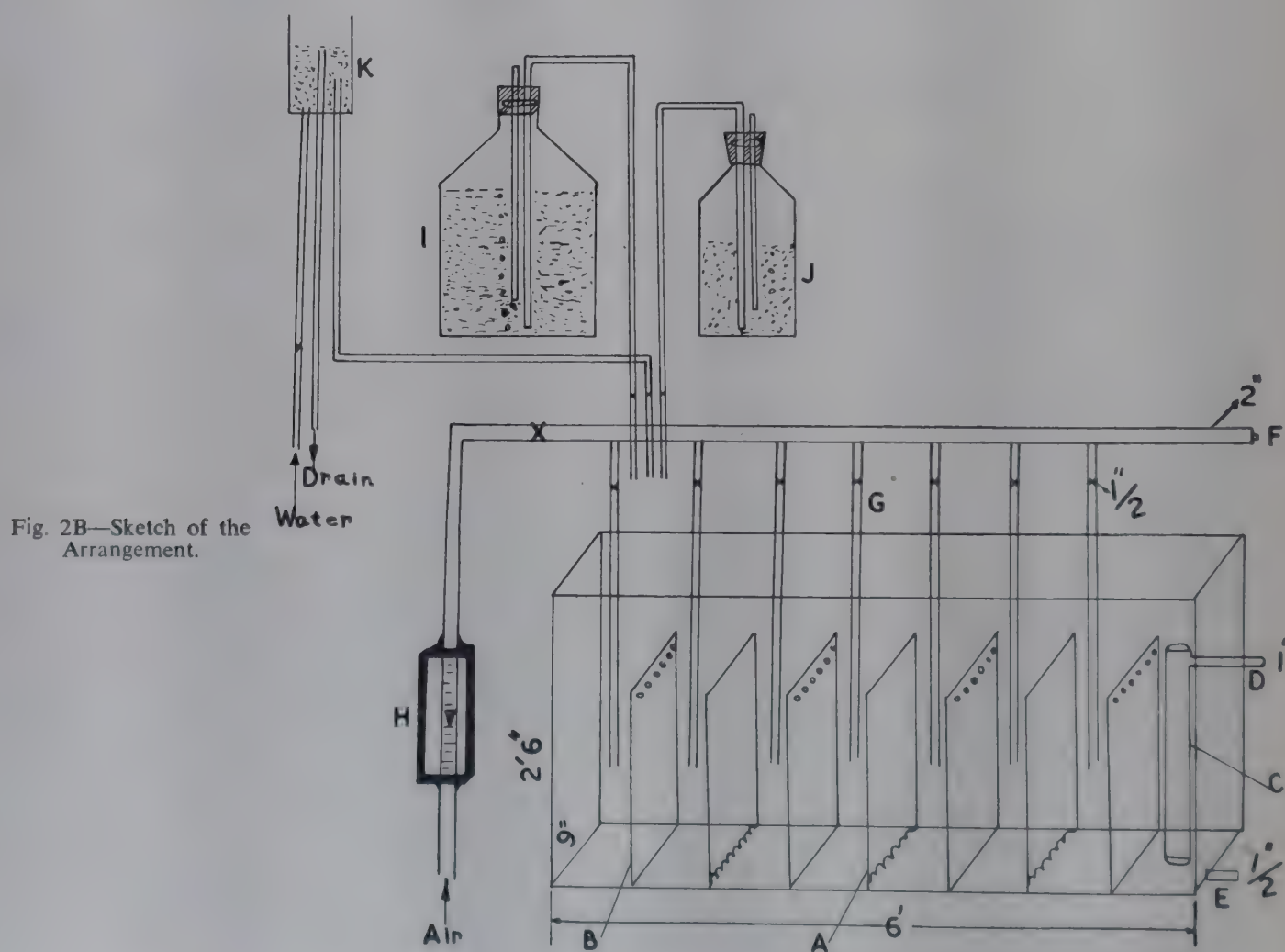


Fig. 2B—Sketch of the
Arrangement.

TABLE 1—BIOLOGICAL OXIDATION OF PHENOL (BENCH-SCALE)
(Air rate maintained at 3 m³/min./m³)

Sl. No.	Temperature range, °C	Phenol Concentration, (mg./l.)	Average Flow Rate, 1/hr.	Detention Time, hr.	Vessel No.	Phenol Concentration (mg./l.) After, hr.				
						0	2	4	6	8
1.	29-32.5	465	0.338	8.9	1	300	332	348	353	327
					2	140	193	204	204	195
					3	11	17	6	17	1
2.	30-33	465	0.375	8	1	6	148	214	260	311
					2	2	20	20	16	20
					3	0	11	0	0	0
3.	30.5-33	500	0.281	10.7	1	24	184	270	307	339
					2	34	50	98	136	184
					3	8	2	18	7	23
4.	30-33	510	0.375	8	1	4	178	265	291	296
					2	6	26	72	92	123
					3	2	6	0	0	0
5.	31-33	510	0.45	6.7	1	224	307	312	327	337
					2	48	124	163	183	200
					3	0	15	20	49	74
6.	40	475	0.30	10	1	38	167	262	313	313
					2	78	50	91	147	162
					3	5	5	8	20	45
7.	39-40	475	0.30	10	1	11	183	281	332	337
					2	17	26	72	143	173
					3	11	8	8	8	2
8.	39.5-40	475	0.40	7.5	1	100	232	313	348	369
					2	11	76	157	217	248
					3	7	5	28	58	86
9.	39.5-40	500	0.50	6	1	9	276	352	373	444
					2	7	113	230	291	337
					3	6	26	100	174	256

the last one are made by 1/2 inch pipes (G) fitted with valves. The total air passed through the system is measured by means of a rotameter (H). The concentrated phenolic liquor (I) and the nutrient mixture (J) are fed into the first compartment separately by a constant-head device. The concentration of phenol is maintained in the desired range by feeding dilution water (K) also in the first compartment by a constant-head device. Separate arrangement for addition of concentrated phenolic liquor and dilution water has been incorporated to avoid storage of large volumes of dilute phenolic liquor.

Starting up of the Plant: At the initial starting of the plant, the vessel was filled with water and phenol-oxidizing bacterial culture from stock and also nutrient solution were added in each compartment. Aeration was started and the addition of phenol was done at regular intervals. This process continued for about 7 days

till the activity of the culture was developed satisfactorily. The activity of the organisms was examined by adding a certain amount of phenol in each compartment and examining the amount of phenol removed after a definite interval.

Results and Conclusion

After satisfactory development of activity in the culture, continuous operation of the plant was started. In the first experiment, the phenol content in the inlet was maintained at 300-400 mg./l. This was done by addition of 2.5 per cent phenol in water in the first compartment at a rate of 5 ml./min. The rate of flow of the dilution water was kept at 410 ml./min. Nutrient mixture was added at a rate of 3-4 ml./min. Air flow-rate was maintained at 3m³/min./m³. Initially samples from each compartment were taken for analysis at an interval of twelve hours, the phenol being estimated by

TABLE 2—BIOLOGICAL OXIDATION OF PHENOL (PILOT PLANT)

Strength of phenol solution	— 2.5%
Water flow-rate	— 410 ml/min.
Air flow-rate	— 3m ³ /min./m ³
Phenol addition rate	— 5 ml./min.
Nutrients addition rate	— 3-4 ml./min.
Temp. range	— 29-34°C

Sl. No.	Sampling interval from Start, hr.	Phenol Conc. in Feed, mg./l.	Phenol Concentration in Different Compartments (1 to 8), mg./l.								Phenol Removal, %
			1	2	3	4	5	6	7	8	
1.	11	356	217	150	133	50	33	6	Nil	Nil	100
2.	24	428	428	400	390	160	140	11	Nil	Nil	100
3.	32	356	283	256	250	178	160	39	22	22	94
4.	40	283	210	160	150	72	56	6	Nil	Nil	100
5.	48	310	150	78	50	28	22	22	11	11	97
6.	58	340	160	33	22	11	6	Nil	Nil	Nil	100
7.	65	344	278	110	94	22	11	Nil	Nil	Nil	100
8.	75	367	250	83	78	56	17	17	17	17	95

modified permanganate method⁴. Thereafter the analysis was conducted at an interval of 8-10 hours. The inlet phenol concentration was determined by collecting the sample from the mixture of concentrated phenol solution and the dilution water fed into the first compartment. It was observed that in course of 6-7 hours almost all the phenol was destroyed. This almost corroborated our data obtained in the bench-scale unit. The results are shown in Table 2 and Fig. 3.

In a second experiment, the phenol concentration in the inlet was gradually increased to 822 mg/l. by increasing the rate of addition of concentrated phenol. With increase in inlet phenol concentration, the effluent from the last compartment showed increasing phenol content particularly after a concentration of 633 mg/l. was reached. With further increase in phenol concentration to 822 mg/l. the removal was found to be only 63 per cent (Table 3) in 8 hours. The rapid increase in phenol concentration seemed to have adversely affected the activity of the culture but on lowering the phenol concentration, the activity had revived.

It is observed from the pilot-plant experiments that with an inlet concentration upto 440 mg./l. phenol could be completely destroyed in about 6-7 hours, which is sufficiently good for any commercial application. Phenolic liquor with higher phenol content could also be treated in the above type of plant by diluting with the inlet feed by recirculation of a part of the effluent from the last compartment. The results of the above experiment being highly encouraging, a large commercial plant

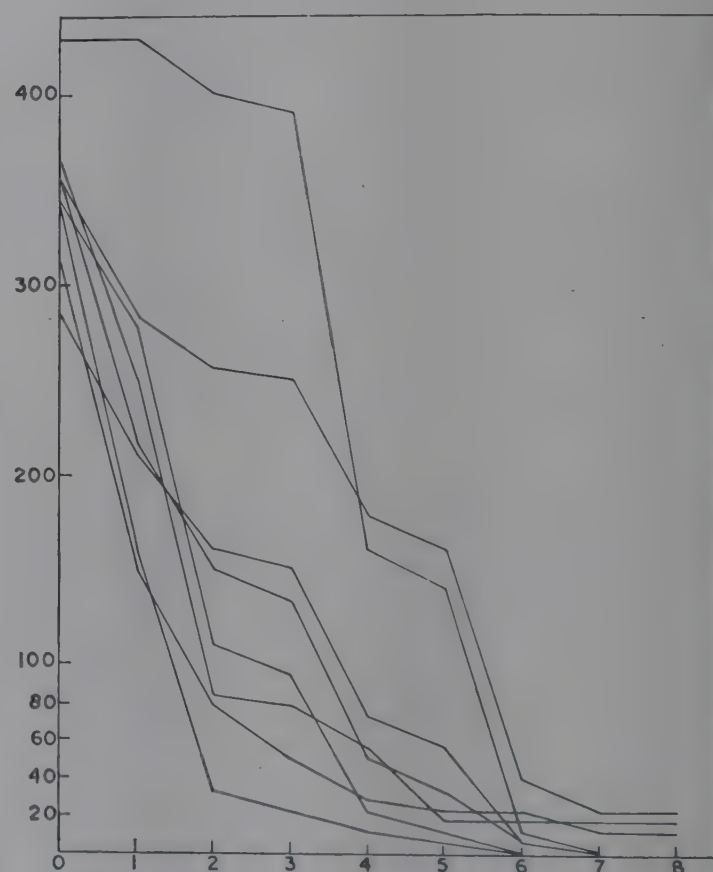


Fig. 3—Biological Oxidation of Phenol.

is being designed to treat the phenolic liquor of a coke-oven plant having a phenol concentration of 400-500 mg./l.

TABLE 3—BIOLOGICAL OXIDATION OF PHENOL (PILOT-PLANT)

Strength of phenol solution — 2.5 %
 Water flow-rate — 410 ml./min.
 Air flow-rate — 3m³/min./m³
 Nutrients addition rate — 3-4 ml./min.
 Temperature range — 30-34.5°C

Sl. No.	Sampling Interval from Start, hr.	Phenol Conc. In Feed, mg./l.	Phenol Concentration in Different Compartments (1-8), mg./l.								Phenol Removal, %
			1	2	3	4	5	6	7	8	
1.	12	410	267	158	156	78	67	9	6	4	99
2.	24	440	350	180	172	75	60	11	9	6	99
3.	36	633	372	228	220	122	114	52	52	52	92
4.	48	822	510	440	428	383	372	322	322	302	63
5.	60	555	300	145	113	60	50	27	22	22	96

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Role of Complexants in Decreasing Phosphate Retention of Soils

By

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The retention of phosphate has been studied in presence of a number of complexants using black and red soil samples collected from the eastern districts of Uttar Pradesh. With addition of a complexant, there is a marked decrease in phosphate retention by these soils; the decrease in phosphate retentive capacity (PRC) is proportional to the amount of complexant added, the only exception being oxalate in which the efficiency decreases at a higher concentration of complexant being added. 8-hydroxyquinoline, ferrocyanide $[\text{Fe}(\text{CN})_6]^{4-}$, citrate and aluminon have been found to be quite efficient in both the types of soil, while EDTA least efficient. The efficiencies of the complexants to inhibit phosphate retention is greater in black soils than in red soils which is directly related to phosphate retentive capacities.

It has been observed that a considerable portion of the added phosphate is retained in aluminium, iron and calcium combinations in soils. Many anions have been found to decrease the activity of aluminium, iron and calcium in soils by "chelation", forming stable complex ions or by forming insoluble precipitation products and thus help in the release of phosphate.

Organic anions such as citrate, tartarate, oxalate, acetate, succinate and inorganic anions such as hydroxyl, fluoride, arsenate, ferrocyanide have been found to reduce phosphorus fixation and assist in the release of native soil phosphate¹⁻⁵. 8-hydroxyquinoline, humic acid, tannin, EDTA, cupferon, aluminon, alizarin, fulvic acid, m-benzyl-phenyl hydroxylamine have also been found to prevent fixation of added phosphorus in varying degrees⁶⁻¹¹. However, such a study for Indian soils is lacking.

The present study was undertaken in order to find out an economic use of added phosphatic fertilizer in soils. Phosphatic fertilizers were employed along with various complexants which are known to react with active phosphate fixers, e.g. aluminium, iron and calcium, in soils and thus prevent the phosphate from fixation loss. A suitable dose of complexant has also been worked out.

Experimental

In the present study, red and black soil samples from the eastern districts of Uttar Pradesh were used. Black soil samples were collected from Ballia and Mirzapur whilst the red soil samples from Mirzapur district.

Procedure: The chemical analysis of soil samples (Table 1) was made according to Jackson¹².

TABLE 1—CHEMICAL COMPOSITION OF SOILS

Soils	Sesquioxides, %	CaCO ₃ , %	Organic Carbon, %	pH	Total P, mg./100 g. Soil
<i>Red Soils of Mirzapur Dt.</i>					
No. 1	5.3	0.87	0.76	6.4	27.75
No. 2	8.6	0.84	0.92	8.2	31.75
No. 3	9.6	0.42	0.70	7.0	33.75
<i>Black Soils of Ballia Dt.</i>					
No. 1	16.7	1.75	0.52	8.0	41.0
No. 2	17.8	1.90	0.60	7.2	53.0
No. 3	17.4	2.15	0.57	7.5	44.0
No. 4	15.7	2.60	0.58	9.0	47.5
<i>Black Soils of Mirzapur Dt.</i>					
No. 1	17.9	2.50	0.48	8.3	37.5
No. 2	23.74	2.60	0.43	8.3	36.25
No. 3	18.85	2.40	0.45	8.3	37.5
No. 4	22.15	2.05	0.39	8.0	40.0

Phosphates in the extracts and leachates were determined colorimetrically using sulphomolybdic acid and chlorostannous reagents¹². 10 ml. of phosphate solutions (KH₂PO₄) containing 50 mg. phosphorus/100 g. soil along with the following complexants (at the rate of 50 and 100 mg./100 g. soil) were added to 1.0 g. soil and kept in contact for 18 hours at room temperature and then filtered: (1) Oxalate as ammonium oxalate; (2) citrate as ammonium citrate; (3) ferrocyanide as potassium ferrocyanide; (4) 8-hydroxyquinoline; (5) aluminon; and (6) EDTA.

The complexants in the filtrates were destroyed by heating with a mixture of nitric and perchloric acids before phosphate estimation. The difference between the amounts of phosphorus added and that present in the filtrates was taken as the amount retained by the known weight of soil.

In order to find out the relative efficiencies of the complexants in decreasing the phosphate retentive capacities (PRC), $\frac{D}{\text{PRC}} \times 100$ values have been worked out, where D denotes a decrease in PRC value due to the addition of the complexant.

Results

Effect of Oxalate Anion: When 50 mg. oxalate/100 g. soil in the form of ammonium oxalate is added, 17.8-28.5

per cent decrease in phosphate retentive capacity (PRC) is observed in case of red soil and 26.3-31.5 and 25.6-35.9 per cent in black soils of Ballia and Mirzapur respectively. As the concentration of oxalate anion is raised from 50 to 100 mg./100 g. soil, the decrease in PRC values ranges from 3.5 to 22.8 per cent for red soil and from 21.0 to 30.2 and 16.2 to 35.9 per cent for the two black soils (Table 2). It clearly indicates that (a) due to the presence of complexant, the decrease is lesser in red soil samples than in both the black soils; and (b) as the concentration of oxalate anion is increased, the relative efficiency of the complexant in decreasing PRC falls off.

Effect of Citrate Anion: When citrate anion is used as a blocking agent for active phosphate fixers in soils, the decrease in PRC values at 50 mg. citrate concentration for red soils ranges from 8.8 to 14.2 per cent and for black soils of Ballia and Mirzapur it ranges between 10.8 to 21.6 per cent respectively. At 100 mg. citrate concentration, the decrease in PRC values is more than 3 times in each case (Table 2). This, therefore, indicates that (a) the efficiency of citrate anion in blocking phosphorus retention in black soils is greater than in red soils; and (b) the decrease in PRC value due to the presence of complexant is proportional to the amount of complexant added. As the concentration of citrate anion is increased from 50 to 100 mg., an one-third to one-fourth decrease is observed in $\frac{D}{\text{PRC}} \times 100$ values.

TABLE 2—ROLE OF COMPLEXANTS IN DECREASING PHOSPHATE RETENTION
[Effect of Oxalate and Citrate]

Soils	PRC	PRC when oxalate		$\frac{D}{\text{PRC}} \times 100$		PRC when citrate		$\frac{D}{\text{PRC}} \times 100$	
	(No complexant)	is added				is added			
		50 mg./ 100 g.	100 mg./ 100 g.	50 mg./ 100 g.	100 mg./ 100 g.	50 mg./ 100 g.	100 mg./ 100 g.	50 mg./ 100 g.	100 mg./ 100 g.
<i>Red Soils of Mirzapur</i>									
No. 1	28.0	23.0	27.0	17.8	3.5	30.0	18.0	—	35.7
No. 2	35.0	25.0	27.0	28.5	22.8	30.0	17.0	14.2	51.4
No. 3	34.0	27.0	32.0	20.6	5.9	31.0	17.0	8.8	50.0
<i>Black Soils of Ballia</i>									
No. 1	43.0	30.0	30.0	30.2	30.2	37.0	23.0	13.9	46.5
No. 2	40.0	28.0	29.0	30.0	27.5	35.0	16.0	12.5	60.0
No. 3	38.0	28.0	30.0	26.3	21.0	31.0	15.0	18.4	60.5
No. 4	38.0	26.0	29.0	31.5	23.6	31.0	19.0	18.4	50.0
<i>Black Soils of Mirzapur</i>									
No. 1	37.0	25.0	32.0	32.4	16.2	33.0	18.0	10.8	51.3
No. 2	39.0	25.0	25.0	35.9	35.9	31.0	19.0	20.5	51.2
No. 3	37.0	24.0	30.0	35.1	18.9	29.0	18.0	21.6	51.3
No. 4	39.0	29.0	26.0	25.6	33.3	34.0	13.0	12.8	66.6

TABLE 3—ROLE OF COMPLEXANTS IN DECREASING PHOSPHORUS RETENTION
[Effect of Ferrocyanide and 8-Hydroxyquinoline]

Soils	PRC	PRC when ferro-		D		PRC when 8-hydroxy-		D	
	(No complexant)	50 mg./ 100 g.	100 mg./ 100 g.	50 mg./ 100 g.	100 mg./ 100 g.	50 mg./ 100 g.	100 mg./ 100 g.	50 mg./ 100 g.	100 mg./ 100 g.
<i>Red Soils of Mirzapur</i>									
No. 1	28.0	26.0	14.0	7.14	50.0	30.0	6.0	—	78.5
No. 2	35.0	31.0	18.0	11.4	48.5	30.0	6.0	14.2	82.8
No. 3	34.0	31.0	15.0	8.82	55.8	35.0	5.0	—	88.2
<i>Black Soils of Ballia</i>									
No. 1	43.0	34.0	17.0	20.9	60.4	37.0	15.0	13.9	65.1
No. 2	40.0	35.0	15.0	12.5	62.5	38.0	14.0	5.0	65.0
No. 3	38.0	35.0	13.0	7.89	65.7	36.0	18.0	5.26	52.6
No. 4	38.0	31.0	11.0	18.4	71.05	31.0	12.0	18.4	68.4
<i>Black Soils of Mirzapur</i>									
No. 1	37.0	33.0	13.0	10.8	64.8	36.0	14.0	2.7	62.1
No. 2	39.0	33.0	8.0	15.3	79.4	36.0	12.0	7.69	69.2
No. 3	37.0	31.0	4.0	16.2	89.1	33.0	10.0	10.8	72.4
No. 4	39.0	29.0	1.0	25.6	97.4	40.0	11.0	—	71.7

Effect of Ferrocyanide Anion ($Fe(CN)_6^{4-}$): This is the most efficient chelating agent because the decreases in the respective PRC values at 50 and 100 mg ferrocyanide anion are 7.14 to 8.82 and 48.5 to 55.8 per cent for red soils, 7.89 to 20.9 and 60.4 to 71.05 per cent for black soils of Mirzapur (Table 3). This shows that (a) the efficiency of ferrocyanide ion in preventing the phosphate retention in black soil is greater than in red soils; and (b) as the concentration of added ferrocyanide ion is increased from 50 to 100 mg./100 g., 3 to 5 times increase in efficiency is observed.

Effect of 8-Hydroxyquinoline (C_9NH_6OH): Next to ferrocyanide ions, 8-hydroxyquinoline is the most powerful complexing agent. The decrease in PRC values at 50 and 100 mg./100 g. concentrations of the complexant ranges from 14.2 and 78.5 to 88.2 per cent respectively for red soils, 5.0 to 18.4 and 52.6 to 68.4 per cent for black soils of Ballia and 2.7 to 10.8 and 62.1 to 72.4 per cent for black soils of Mirzapur respectively (Table 3). This clearly indicates that (a) the efficiency of 8-hydroxyquinoline in decreasing phosphorus retention is greater in red soils than in black soils and (b) 6 to 9 times increase in blocking efficiency is observed with increase in concentration of added complexant from 50 to 100 mg./100 g.

Effect of Aluminon: When aluminon is used as a chelating agent along with soluble phosphates, a decrease

in PRC values is observed. At 50 mg./100 g. aluminon concentration, the decrease in PRC values ranges from 0 to 5.71 per cent in red soils and 2.5 to 13.9 and 2.7 to 17.9 per cent for black soils of Ballia and Mirzapur respectively. When the concentration is raised to 100 mg., these values are shifted to between 38.23 to 53.57, 26.31 to 47.37 and 40.5 to 59.46 per cent for red soils and black soils of Ballia and Mirzapur respectively (Table 4). This indicates that: (a) the efficiency of aluminon increases with increase in its concentration; and (b) there is no specific difference in blocking efficiency in red and black soils.

Effect of EDTA: It is observed that the relative efficiency of EDTA is less in decreasing PRC of soils in comparison to other complexants used. The decreases in PRC at 50 mg. concentration range from 5.71 to 5.88, 7.5 to 18.6 and 2.7 to 15.38 per cent for red soils and black soils of Ballia and Mirzapur respectively. At 100 mg. concentration, these values are raised in the range of 14.28 to 22.85, 22.5 to 44.73 and 8.18 to 30.76 per cent respectively (Table 4). This shows that: (a) the efficiency of EDTA in black soils is greater than in red soils, and (b) the decrease in PRC is proportional to the amount of EDTA added.

It can, therefore, be concluded that (1) when a complexant is added, there is a marked decrease in PRC of soils; (2) the decrease in PRC is proportional to the

TABLE 4—ROLE OF COMPLEXANTS IN DECREASING PHOSPHORUS RETENTION

[Effect of Aluminon and EDTA]

Soils	PRC (No complexant)	PRC when aluminon is added		D PRC $\times 100$		PRC when EDTA is added		D PRC $\times 100$	
		50 mg./ 100 g.	100 mg./ 100 g.	50 mg./ 100 g.	100 mg./ 100 g.	50 mg./ 100 g.	100 mg./ 100 g.	50 mg./ 100 g.	100 mg./ 100 g.
<i>Red Soils of Mirzapur</i>									
No. 1	28.0	28.0	13.0	0.	53.57	32.0	24.0	—	14.28
No. 2	35.0	33.0	16.0	5.71	54.28	33.0	27.0	5.71	22.85
No. 3	34.0	34.0	21.0	0	38.23	32.0	27.0	5.88	20.58
<i>Black Soils of Ballia</i>									
No. 1	43.0	36.0	25.0	13.9	41.86	35.0	33.0	18.60	23.25
No. 2	40.0	39.0	26.0	2.5	35.00	37.0	31.0	7.5	22.50
No. 3	38.0	36.0	28.0	5.26	26.31	38.0	27.0	0	22.94
No. 4	38.0	33.0	20.0	13.1	47.37	35.0	21.0	7.88	44.73
<i>Black Soils of Mirzapur</i>									
No. 1	37.0	36.0	22.0	2.7	40.54	33.0	28.0	10.81	24.32
No. 2	39.0	37.0	22.0	5.12	43.58	36.0	29.0	7.69	25.64
No. 3	37.0	35.0	15.0	5.45	59.46	36.0	34.0	2.70	8.18
No. 4	39.0	32.0	17.0	17.9	56.40	33.0	27.0	15.38	30.76

amount of complexant added, the only exception being ammonium oxalate in which the efficiency decreases at higher concentration; (3) the efficiency of the complexants to inhibit the phosphate retention in black soils is greater than in red soils. Simultaneously the retention of phosphorus in black soils is also higher; and (4) the efficiencies of the complexants to inhibit the retention of phosphate by red and black soils can be written in the following decreasing order.

Soils	50 mg./100 g. soil concentration	100 mg./100 g. soil concentration
Red soils	Oxalate > 8-hydroxy- quinoline > ferrocyanide > aluminon > EDTA	8-hydroxyquinoline > aluminon > citrate > ferrocyanide > EDTA > oxalate.
Black soils	Oxalate > citrate > ferro- cyanide > 8-hydroxy- quinoline > aluminon = EDTA	Ferrocyanide > 8-hydroxy- quinoline > citrate > aluminon > EDTA* > oxalate *EDTA stands at the end in Mirzapur black soil

It is observed that oxalate at lower concentrations is most active whereas at higher concentration it is least active. 8-hydroxyquinoline, ferrocyanide, citrate and

aluminon have been found quite efficient in almost both the soils as they show a quite significant decrease in PRC at both concentrations. EDTA shows a lesser decrease in PRC in almost every case.

Discussion

When a soluble phosphate is added to soils, the phosphate ions react with their constituents, such as iron, aluminium and calcium, which are supposed to be the most active phosphate fixers in them. When the soluble phosphates are added with complexants in soils, there is a competition between phosphate anions and complexants (either as such or in anionic form) to react with iron, aluminium and calcium. As the complexants have a greater affinity for certain of the soil constituents, they form stable complexes (either soluble or insoluble) with iron, aluminium and calcium of soils and thus reduce the possibility of H_2PO_4^- ions to be held in their combinations. This results in a direct decrease of PRC values of soils.

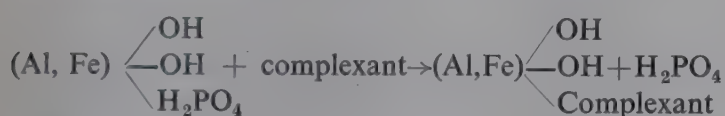
Of the complexants used, some have a high chelating power for iron, viz. ferrocyanide, others for aluminium, viz. aluminon, yet there are some others, like 8-hydroxyquinoline and citrate, which have chelating power for both iron and aluminium; and finally there are those like EDTA and oxalate, which chelate iron, aluminium and calcium simultaneously. Consequently, when one

or the other complexant is used along with the soluble phosphates, the soils exhibit reduced PRC values. However, the reduction in PRC can be expected to be more only if the added complexant chelates with the very constituents of a soil with which added phosphorus combines.

Aluminon is a complexant which chelates with aluminium alone and hence the decrease in PRC due to its addition can be claimed to be due to an inhibition in the formation of aluminium phosphate in soils.

8-hydroxyquinoline and ferrocyanide can form chelates with both iron and aluminium and hence the reduction in PRC will be due to the formation of aluminium and iron phosphates in soils.

As the retained phosphorus exists mostly in aluminium phosphorus and iron-phosphorus combinations, the highest efficiency of 8-hydroxyquinoline and ferrocyanide in decreasing PRC can directly be related to the chelation of aluminium and iron and a subsequent decrease in aluminium-phosphorus and iron-phosphorus combinations. The mechanism can be expressed by the following equation:



The complexants which can chelate with more than two constituents of soil simultaneously, generally exhibit a poorer effect in decreasing PRC. The best example is EDTA; the reason for low efficiency of this complexant may be due either to its multifarious activities or its small concentration added.

Hence, it is concluded that these complexants, which can chelate aluminium and iron simultaneously, produce better results in decreasing retention of added phosphorus than those which can form complex with aluminium or iron singly or which chelate with more than two constituents.

The presence of complexants in the soils or their introduction along with applied phosphorus may help in keeping more of phosphorus in the water-soluble state, thereby helping increased availability of phosphorus to the plants. However, a high concentration of complexants needs to be present.

The study with complexants also throws some light on the probable combinations in which retained phosphorus can exist in soils.

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Beneficiation of Rajasthan Rock Phosphate

By

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A laboratory-scale method has been developed for the beneficiation of rock phosphate located in Jaisalmer area of Rajasthan. It consists of calcining the rock phosphate—which contains a considerable quantity of calcium carbonate—at 950 to 980°C and quenching and leaching the mass in water from a cooling tower in a fertilizer plant. The P_2O_5 in the samples could be enriched from 27.35 to 40.96 per cent and from 11.17 to 17.11 per cent.

Recently some sizeable deposits of rock phosphate have been located by the Geological Survey of India¹ in the Jaisalmer area of Rajasthan. The rock phosphate is of a comparatively lower grade and contains a high percentage of calcium carbonate as impurity. Apart from the lower phosphate content, the presence of high calcium carbonate in it renders it unsuitable for the manufacture of phosphoric acid and phosphatic fertilizers, because of the higher consumption of acid in neutralizing the carbonate. Since the carbonate is held firmly in the matrix of the rock, the conventional methods of beneficiation cannot be applied in this case. A method has been developed in this laboratory for upgrading this rock phosphate by removing substantially calcium carbonate from it.

The rock phosphate samples (Table 1) received in the

form of lumps and in small pieces were crushed and then ground to pass through 100 mesh (B.S.) sieve. A weighed amount of the powdered material was next heated at 950 to 980°C in a sillimanite crucible inside a muffle furnace for 2 hours and then quenched in water. The quenched mass was then heated in the same water for 15 to 20 min. at 70°C with continuous stirring. The mass was then allowed to settle and the clear liquid decanted. The residual phosphatic material was filtered out, rinsed with hot water at 70°C and finally dried at 100°C. Two samples of water were used in these studies. One was process water from the water treatment plant and the other was water from the cooling tower of the gas reforming plant at Sindri. The analyses of water samples are given in Table 2.

It can be seen that there is an increase in the P_2O_5 content of the original rock phosphate sample after ignition at 950-980°C with an enrichment of 26.03 and

TABLE 1—ANALYSIS OF ROCK PHOSPHATE SAMPLES FROM JAISALMER (RAJASTHAN)

Ingredients	Sample A, %	Sample B, %
SiO_2 +Insoluble	4.92	27.09
$Fe_2O_3+Al_2O_3$	1.69	11.56
CaO	45.50	38.66
MgO	0.08	0.05
SO_3	1.15	0.05
NaCl	0.95	0.06
P_2O_5	27.35	11.17
CO_2	11.63	8.17
F	4.35	2.12
Moisture	1.05	0.49
Loss on ignition at 950°C for 2 hr.	26.07	11.76
P_2O_5 in calcined rock	34.47	13.15

TABLE 2—ANALYSIS OF WATER SAMPLES

Ingredients	Cooling Tower Water	Process Water
$Fe_2O_3+Al_2O_3$	45 ppm	5 ppm
NH_3	100 "	1 "
Cl	82 "	65 "
P_2O_5	20 "	nil
T.D.S.	530 "	206 ppm
SO_3	140 "	39 "
CaO	50 "	40 "
P	nil	nil
M	70 ppm	86 ppm
pH	5.50	6.30

TABLE 3— P_2O_5 IN QUENCHED AND LEACHED SAMPLES

Samples	Amount Quenched in 100 ml. water, g.	P_2O_5 in Leached Rock- Phosphate, %	
		With Cooling Tower Water	With Tap Water
Sample A	1	40.96	34.46
	2	39.07	34.30
	3	38.96	35.07
	4	38.69	35.04
	5	38.32	35.07
	6	38.23	—
	8	35.76	—
	10	34.34	—
Sample B	1	17.11	13.79
	2	15.69	13.25

13.75 per cent in the cases of samples A and B respectively (Table 1). The percentage enrichment in the case of sample A is more because it contains more of carbonate and less of silica in comparison to sample B. On leaching those samples in the cooling tower water after quenching, there is a further increase in the P_2O_5 content of the material (Table 3). The maximum enrichments of P_2O_5 contents in samples A and B were of 40.96 and 17.11 per cent respectively. There was, how-

TABLE 4—DISSOLVED CaO IN WATER EXTRACTS OF CALCINED ROCK PHOSPHATE SAMPLE A

Serial No.	Quenched in 100 ml. water, g.	Dissolved CaO, mg./l.	
		In Cooling Tower Water	In Process Water
1	0	50	40
2	1	184	42
3	2	198	46
4	3	213	38
5	4	218	34
6	5	226	39
7	6	240	—
8	7	254	—
9	8	254	—

ever, no appreciable enrichment in P_2O_5 content when the calcined sample was further quenched in process water. The better effect of the cooling tower water in enriching the P_2O_5 content in the phosphate samples is due to its greater power of dissolving out calcium oxide from the calcined mass. This will be clear from the comparative figures (Table 4).

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Some Studies on Protective Coatings for Use in Fertilizer Plants

By

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Studies on paints and protective coatings, such as enamel, chlorinated rubber, aluminium and bitumen black were made in the laboratory as well as under actual plant conditions to find out the suitability of coatings for corrosive environments that prevail in fertilizer plants. Bitumen black and aluminium paints on red oxide/zinc chromate primer were found suitable at the plants.

Introduction

Corrosion of metallic structure and equipment is a major problem in fertilizer plants.¹ Various measures are taken to minimize it, and one of the most important of these is the use of protective coatings. Since conditions are different in different plants and also in different areas of the same plant, selection of proper protective coatings is of prime importance.

The present paper deals with laboratory and field tests with some coatings with a view to assess their suitability for protecting structural steel in some areas of the fertilizers factory at Sindri. The different plant locations are described below.

(1) *Urea Prilling Tower*: The tower is meant for making globules from a highly concentrated solution of urea (95-98 per cent) at a temperature between 130 and 140°C. The highly concentrated solution of urea is allowed to fall from a height of about 50 metres in the form of a shower and comes in contact with counter-current air produced by the natural or induced draft which facilitates the formation of globules. The mild steel structures at this location suffer from corrosion due to the deposition of urea and also of ammonium sulphate nitrate and gypsum, since the tower is very close to gypsum grinding plant and storage section and also to ammonium sulphate-nitrate plant.

(2) *Catalyst Manufacturing Plants*: The mild steel structures in this plant come in contact with corrosive solids, solutions and vapours e.g. ferrous sulphate,

ammonia, steam, etc., and the corrosion is severe. The selection of the protective coating for such a plant condition is difficult unless some field trials are made.

Experimental

Mild steel panels 3"×6" were degreased and derusted and the surfaces were given phosphate treatment. Primers and other different types of paints were collected from various manufacturers according to their recommendations. Along with these samples, one bitumen paint formulated and prepared in this laboratory was also taken for consideration. All the panels were given two coats of red oxide/zinc chromate primer* before the application of top coats, as this primer was found most suitable in contact with most fertilizer materials. Only in cases of chlorinated rubber-base paint and bituminous black paint II, no primer was used as advised by suppliers.

Before the laboratory and field tests, the panels were allowed to dry for seven days in the laboratory and the film thicknesses were measured. Two top coats of the finishing paint, e.g. aluminium, grey, green, bituminous black, etc., were then applied on the priming coat. Panels were suspended in a 3 per cent solution of ammonium sulphate, ammonium sulphate nitrate, sodium chloride and urea under laboratory conditions for two weeks and day to day observations were made²⁻⁴.

*in accordance with Indian Standards Specification 2074.

TABLE 1—RESULTS OF THE LABORATORY TESTS

Sample	Thickness, mils	Sodium Chloride, 3% Soln.	Ammonium Sulphate, 3% Soln.	Ammonium Sulphate Nitrate, 3% Soln.	Urea, 3% Soln.
Green Enamel	3.5	Minute blistering throughout panel in one week; becomes more severe with sign of corrosion thereafter.	Blistering with sign of corrosion in 7 days.	Blistering with sign of corrosion in 7 days.	No appreciable change in one week; blistering at several places in 14 days.
Chlorinated Rubber-based Grey Paint	2.5	A few small blisters at places which become more with sign of corrosion in 4 days.	Small blisters with sign of corrosion by 7 days.	Small dense blisters with sign of corrosion by 7 days.	Few moderate sporadic blisters by 14 days.
Aluminium Paint Z	3.5	—	—	—	Very few minute blisters at places by 14 days.
C	3.5	—	—	—	Very few small blisters throughout the panel by 14 days.
I	3.0	—	—	—	Moderate blisters by 14 days throughout the panel.
Bitumen Black I	3.5	No change in one week but change in gloss in 14 days	A few small blisters at places; remain same for 14 days	Moderate blisters at places during 14 days	No change during 14 days
Bitumen Black II	4.0	No change in 7 days but blistering with sign of corrosion at places during 14 days	Sign of corrosion at places during 14 days	Sign of corrosion at places during 14 days	No change during 14 days

Note: Z, C and I: These are three aluminium paints from different manufacturers.
 Bitumen Black I is paint formulated in this laboratory.
 Bitumen Black II is a mat finish thixotropy paint.

TABLE 2—RESULTS OF THE EXPOSURE TEST AT PLANTS

Sample	Thickness mils	Urea Prilling Tower	Catalyst Manufacturing Plant
Green Enamel	3.5	Loss in gloss, moderate blisters throughout the panel after one month; film becomes soft in 5 months.	Not satisfactory. Failed in 2 months.
Chlorinated Rubber-based Grey Paint	2.5	Sign of corrosion at several places on the panel in 2 months.	No appreciable change in 2 months.
Aluminium Paint Z	3.5	No appreciable change in 4 months	Slight loss in gloss in 4 months.
C	3.5	Appreciable change in gloss with few small blisters in 4 months.	Appreciable change in gloss and becomes grey in 4 months.
I	3.0	Appreciable change in gloss with blisters throughout the panel in 4 months.	Change in gloss and practically becomes grey with dense small blisters in 4 months.
Bitumen Black I	3.5	Slight loss in gloss in 4 months.	No change during 4 months.
Bitumen Black II	4.0	Corrosion at several places in 4 months.	No change during 4 months.

Similarly, the panels were also exposed at the plant locations and observations were made at intervals of one month.

Discussion

Laboratory Tests: It can be seen that no paint has been found completely satisfactory under the drastic accelerated tests performed in the laboratory (Table 1). In urea solution, the damage is much less as compared to that in the fertilizer salts and sodium chloride. Among the paints studied, bitumen black showed better performance which can be termed satisfactory.

Field Tests: The field tests were carried out at the Sindri Plants. It will be observed (Table 2) that the performance of the green enamel paint has been very poor in the urea prilling tower. The chlorinated rubber-based paint failed at the prilling tower but showed somewhat better performance at the catalyst manufacturing plant. The aluminium paints—specially the type Z—were found satisfactory both at the prilling tower and the catalyst plant; among the other two paints C was found better than I whose performance was

extremely poor. Bitumen black I was found satisfactory at both the places, while bitumen black No. II was found suitable at the catalyst plant but failed at the prilling tower.

Judged on an overall basis, there is a fair degree of agreement between the laboratory and field exposure tests. Bitumen black and aluminium paint on zinc chromate/red oxide primer were found suitable at the plants.

The results reported in this paper will be helpful for the selection of protective coatings for different plants and for different corrosive environments. Further studies are being carried out so that more data can be accumulated for the proper guidance of plant maintenance personnel.

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Indirect Method of Estimation of Phosphorus by Atomic Absorption Spectrophotometry

By

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A quick and accurate method for phosphorus determination in rock phosphate has been developed by atomic absorption spectrophotometry. Phosphorus is determined by observing the depression in absorbance of strontium caused due to its presence.

Introduction

The direct estimation of phosphorus by atomic absorption spectrophotometry is not possible because of the instrumental limitations as the resonance line of phosphorus lies in the vacuum ultraviolet region. The indirect method¹, based on the gravimetric estimation of phosphorus, involves the same number of chemical operations. Zaugg^{2,3} has estimated phosphate

in biological materials by determining molybdenum in phosphomolybdic acid and extended the method for determination of phosphate in natural and sea waters.

The present method is also an indirect one based on the interference of phosphorus on alkaline-earth elements. This, though a great handicap in estimation of alkaline-earth elements, has been utilized here for determining phosphorus in rock phosphate. David⁴

has observed the depressing effects of phosphate, silicate, aluminium and sulphate on the absorbance of strontium. He observed a very little depression by phosphate alone but together with calcium the effect was very much prominent. Therefore, he removed the phosphate ion by passing the sample through a column containing an anion-exchange resin. We observed that the depression in strontium is sufficient to be utilized for phosphorus estimation. Trent and Slavin⁵ have studied the effect of hydrochloric and nitric acids, glycerine, $(\text{PO}_4)^{3-}$ etc. on the absorbance of strontium and, in most cases, they observed a depression. In the case of hydrochloric acid, only a gross amount of the acid has an appreciable effect on the absorbance. They also found that alkali metals in general, enhance the strontium absorbance. The same has been observed in the case of calcium also by earlier workers⁶.

In flame emission photometry a similar effect was also observed, which has been used for the determination of phosphorus by Dipple⁷ et al. This is true in case of atomic absorption spectrophotometry as well. Dipple⁷ et al have used calcium in the estimation of phosphorus, but in this study strontium has been chosen because strontium hollow cathode lamp is found to be more stable than the calcium lamp. However, calcium could also have been used.

Since strontium absorption is affected by the anions, such as $(\text{NO}_3)^-$, $(\text{SO}_4)^{2-}$ and a gross amount of Cl^- , and certain cations e.g. sodium, potassium and aluminium, etc., it was necessary to remove these from the samples. The cations were removed by using the cation-exchange resin (Amberlite IR-120) and the solution is made in the minimum amount of hydrochloric acid. 60 ppm strontium carbonate was added in all the samples to keep the concentration of strontium carbonate at 30 ppm. ($\text{Sr}=17.8$ ppm).

Experimental

Sample Preparation: 0.1 g. of the rock sample was digested in 10 ml. hydrochloric acid and 5 ml. nitric acid. It was heated gently for 30 minutes and then evaporated to dryness and heated to dehydrate the silica. The dried portion was then taken in 1 ml. of concentrated hydrochloric acid and filtered. The filtrate was passed through the ion-exchange column containing Amberlite IR-120 (H^+) resin*. It was then washed by 100 ml. of 0.015 N hydrochloric acid to avoid the precipitation of iron and aluminium phosphates⁸ and then distilled

*Prepared by washing Amberlite IR-120 (Na^+) with 4N hydrochloric acid.

water was added to make the volume 250 ml. This solution was diluted 10 times to bring the phosphate concentration in the linear range of the working curve. It was further diluted 1:1 with 60 ppm strontium carbonate solution, which is prepared by using minimum amount of hydrochloric acid. Four rock phosphate samples were prepared in the above manner.

Procedure: The standard solution of 200 ppm phosphorus was made by dissolving 0.5916 g. of di-sodium phosphate in about 50 ml. distilled water. It was passed through the same cation-exchange column and all the operations as in the case of sample preparation were repeated. The final solution was made to 250 ml., which was diluted 10 times to get a phosphorus standard of 20 ppm.

10 ml. of 60 ppm strontium carbonate solution was taken and 10 ml. of phosphorus standard and distilled water suitably added to get a phosphorus concentration in the solutions in the range of 0 to 10 ppm.

The Perkin-Elmer model 303 atomic absorption spectrophotometer with DCR-1 attachment in combination with an air-acetylene flame and the Perkin-Elmer hollow cathode lamp were used. The operating conditions used were same as given in Analytical Method for Atomic Absorption Spectrometry.¹

Observations and Results

The effect of phosphorus on strontium absorbance is shown in Fig. 1. It has been observed that for 30 ppm strontium carbonate solution (17.8 ppm Sr), the depression effect of phosphorus on strontium absorbance is

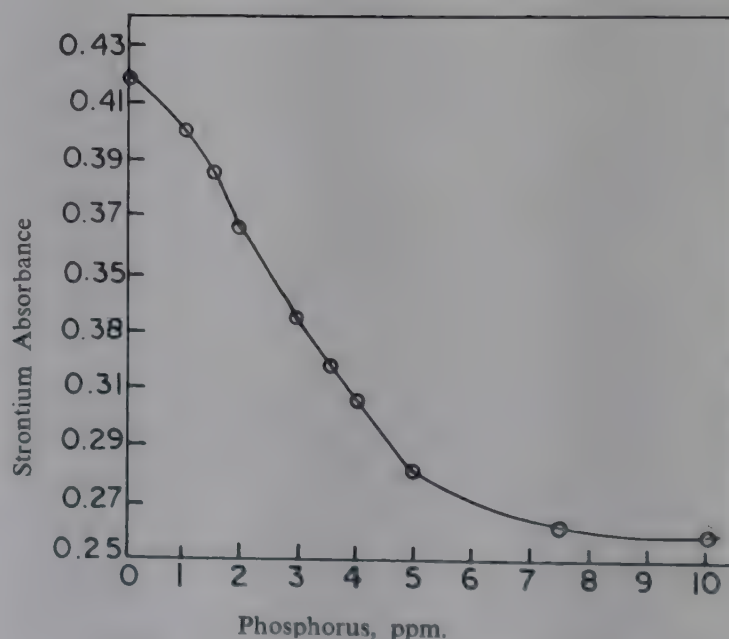


Fig. 1—Calibration Curve for Phosphorus.

linear upto 6 ppm of phosphorus, and subsequent addition of phosphorus does not cause any further depression. The linear part of the curve from 0 to 5 ppm phosphorus was utilized to estimate phosphorus in the samples.

Some observations were taken by changing the fuel flow while keeping the air flow fixed. It has been observed that there was a significant loss of sensitivity (as the strontium absorbance decreases) in the oxidizing flame. The saturation value of phosphorus, however, remains the same. Our values (Table 1) are in good agreement with the results available from other sources.

TABLE 1—VALUES OF P_2O_5 CALCULATED FROM OBSERVATIONS

Rock Phosphate Sample	P_2O_5 , %
RP ₁	28.05
RP ₂	25.19
RP ₃	25.76
RP ₄	28.06

Discussion

The saturation part of the working curve (Fig. 1) is suggestive of some equilibrium being reached which prevents the availability of any more free strontium atoms in the ground state to the flame. It is, therefore, surmised that the equilibrium is perhaps due to the formation of some phosphorus compound of strontium, which is quite stable at the flame temperature.

In addition to the fact that it is less time-consuming, our method is a definite improvement over the existing atomic absorption method in which molybdenum is

estimated in the phosphomolybdate complex. As observed by Trent⁵ et al, the gross concentration of hydrochloric acid only affects the strontium determination; therefore a sample containing little hydrochloric acid can be determined without any interference. The effect of $(NO_3)^-$ can be avoided by suitable sample preparation. The working range can be extended by increasing the strontium concentration in the oxidizing flame.

This study can be adopted for phosphorus determination in water, steel and biological samples etc. Further studies on phosphorus estimation are in progress.

Acknowledgements

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A Magnetic Field Marker for Use With ESR Spectrometers

By

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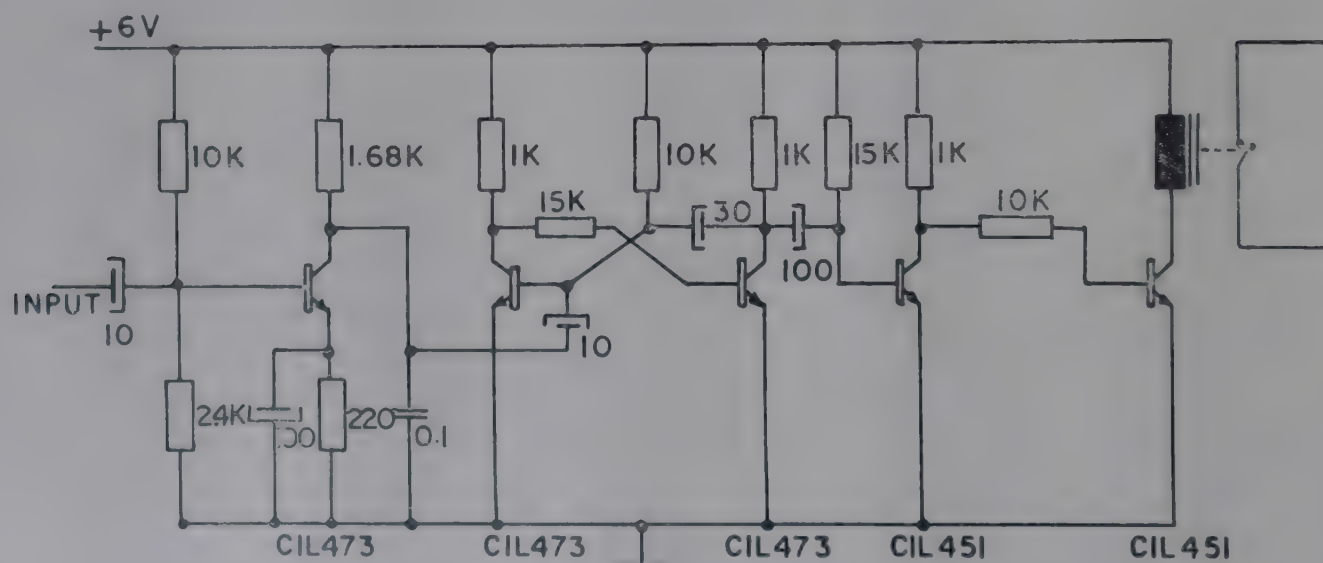
A simple automatic device, employing only indigenous components, has been developed for automatic marking on the resonance recorder. It can be adapted for use on any ESR spectrometer.

While studying narrow ESR spectra, as arising from free radicals, it suffices to measure the magnetic field strength at one or two points only, and such measurements may be made under static conditions without much inconvenience. But in studying multicomponent systems, such as industrial catalysts, where a wide range of g -values may be encountered, a very large field sweep is necessary. In such cases, some device to measure the field strength, while it is being swept, must be used.

Proton resonance gaussmeters are invariably used for precise field measurements. Though it is possible to observe the proton resonance signal on an oscilloscope and activate a marker device manually, a time lag, determined by personal factors, inevitably comes in and

causes inaccuracy in the measurement. To eliminate such inaccuracies, an automatic marking device is much more desirable. A very simple circuit, employing only indigenous components is described here, which was successfully employed by the authors for automatic marking of the resonance positions on the ESR recorder, and which can be adapted easily for use on any ESR spectrometer.

The operating conditions relevant for the design are: (1) The peak height of the signal from the gaussmeter is about 100 mV; (2) the field modulating coils of the gaussmeter produce an amplitude continuously variable between 0 and 25 gauss, the modulation frequency being 50 Hz (mains frequency); (3) due to the com-



Circuit Diagram

paratively high modulation frequency, considerable "ringing" is present in the proton resonance signal; (4) the time constant of the spectrum recorder at the most frequently used damping setting is 3 seconds for a 12 cm. pen travel.

So, to produce a one cm. mark on the chart, a square pulse of 0.25 sec. duration must be applied to the recorder. The circuit should then consist of a suitable pulse shaper and amplifier circuits.

An event marker press button switch is already incorporated in the recorder. The simplest solution, therefore, was to place a normally open relay contact in parallel with the event marker switch and to actuate the relay by the proton resonance signal.

To obtain the requisite pulse duration and shape, a monostable gating circuit having a time constant of 0.3 sec. was used. The trigger level of this circuit was about 1.2 volts, so that a preamplifier of gain 12 was

necessary to enable the proton signal to trigger the gate. A single stage amplifier, having a gain figure of 15 was found sufficient.

The output of the monostable circuit was fed to a driver stage, which in its turn switched the power stage on or off. The relay coil was used as the collector load of the power stage. The modulation amplitude of the gaussmeter was adjusted to suit the field sweep rate in order to avoid multiple marking.

Indian made silicon planar n-p-n transistors were used throughout and the relay used was an ordinary telephone relay having a coil resistance of 200 Ohms and operating current of 30 mA.

Acknowledgement

The authors are grateful to Dr. B. K. Banerjee, Additional Superintendent, for his interest in the work.

Determination of Some Trace Impurities in Drinking Water by Atomic Absorption Spectrophotometry

By

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Atomic absorption spectrophotometry has been used for the estimation of trace quantities of chromium, lithium, cobalt, manganese, copper, lead, iron, barium, zinc, potassium, magnesium, sodium and calcium in drinking water of Sindri.

The discharge of industrial effluents into the *Damodar* river may cause pollution in drinking water of Sindri. Keeping this in view the drinking water samples of Sindri township have been collected on various dates and analysed by atomic absorption spectrophotometer for metallic impurities.

Sample Preparation

Samples were collected in polythene bottles and a little

hydrochloric acid was added to them. For the determination of zinc, a direct sample was used but for potassium, sodium, magnesium and calcium the samples were diluted ten times to bring the concentration of these elements in the working range of the instrument. As the concentration of chromium, lithium, cobalt, manganese, copper, lead, iron and barium was very low and was not possible to determine directly, the samples were concentrated 30 times by evaporating on a hot plate.

TABLE 1—CONTENTS OF SOME TRACE IMPURITIES IN THE DRINKING WATER AT SINDRI, ppm

Sam- ple No.	Cr	Li	Co	Mn	Cu	Pb	Fe	Ba	Zn	K	Mg	Na	Ca
1.	0.0009	0.0021	0.0077	0.022	0.037	0.082	0.328	0.413	0.575	2.90	7.60	11.35	19.7
2.	0.0006	0.0023	0.0077	0.019	0.039	0.081	0.333	0.430	0.200	2.25	6.55	9.95	15.5
3.	0.0007	0.0022	0.0075	0.010	0.023	0.097	0.152	0.430	1.600	2.65	6.60	10.55	17.2
4.	0.0020	0.0020	0.0073	0.061	0.025	0.067	0.517	0.430	0.815	2.60	6.70	10.80	17.5
5.	0.0009	0.0021	0.0074	0.033	0.026	0.102	0.300	0.433	0.200	2.70	6.40	10.45	17.0
6.	0.0017	0.0022	0.0058	0.014	0.010	0.067	0.100	0.367	0.100	3.50	6.95	12.00	17.7
7.	0.0009	0.0022	0.0057	0.013	0.007	0.060	0.177	0.200	0.087	2.80	7.30	11.25	17.2
8.	0.0009	0.0023	0.0067	0.028	0.013	0.060	0.293	0.330	0.565	2.90	7.50	11.25	17.0
9.	0.0017	0.0019	0.0073	0.010	0.014	n.d.	0.135	0.307	0.340	2.70	6.40	10.45	15.2
10.	0.0014	0.0018	0.0065	0.010	0.018	n.d.	0.327	0.273	0.425	2.45	5.70	10.15	14.2
Max. Allowable limit	0.05	—	—	0.5	1.5	0.1	1.0	1.0	15	—	150	—	200

— Values not available.

n.d. Not detected.

Instrument and Procedure

Perkin Elmer Model 303 Atomic Absorption Spectrophotometer equipped with a digital concentration readout accessory (DCR—1) and power supply for discharge lamps was used.

The analytical conditions were used as suggested by Perkin Elmer¹. Various samples and corresponding standard solutions were aspirated in air-acetylene flame, and the absorbance values obtained were plotted against concentration. The quantities of various elements were noted from the graphs. The results are given (Table 1) along with the maximum allowable limits in accordance with the international standards for drinking water².

Discussion

For determination of impurities present in water samples, different methods are available but the present

method is comparatively rapid and accurate for very low concentration of different elements. From the present work it has been found that the maximum concentrations of all the determined elements are well within the maximum allowable limits for drinking water.

Acknowledgement

The authors' thanks are due to Dr. K. R. Chakravorty, General Manager, for his keen interest in this work. Thanks are also due to Dr. B. K. Banerjee for his constant encouragement in course of their work.

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On Calcium and Strontium Hydroxyapatites

By

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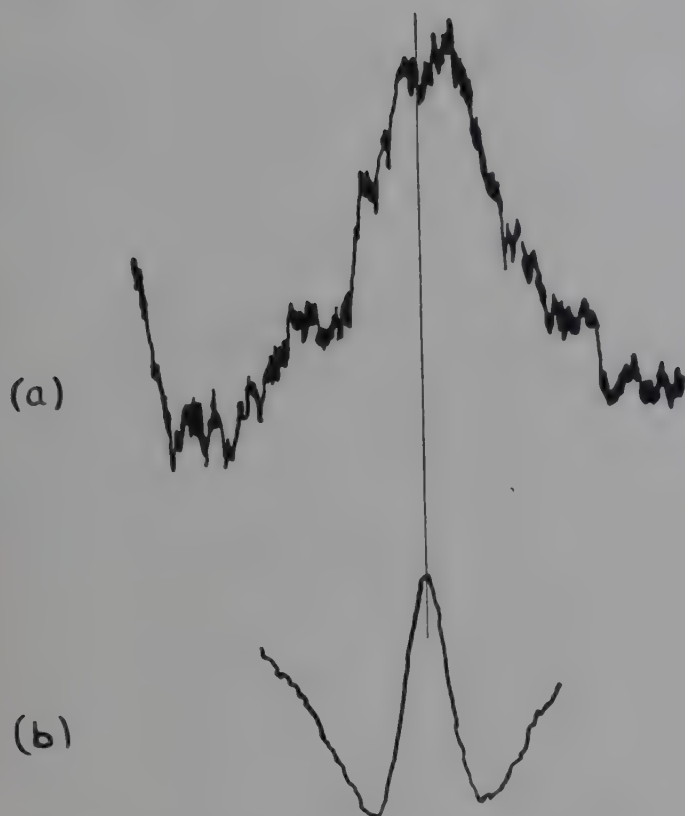


Fig. 1—Wide-Line Nuclear Magnetic Resonance Spectrum of Calcium Hydroxyapatite.

- (a) Spectrum of Calcium Hydroxyapatite
(b) Reference Signal from 85% Phosphoric Acid

The calcium and strontium hydroxyapatites were subjected to wide-line nuclear magnetic resonance spectra¹ (Figs. 1 and 2). The chemical shift of the phosphorus resonance was measured, and it was found that in the case of calcium hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, the p^{31} signal was shifted upfield 40 ppm relative to that of the reference signal from 85 per cent phosphoric acid. In the case of the strontium hydroxyapatite, $\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2$, however, no distinguishable shift relative to 85 per cent phosphoric acid was evident. The line width measured for the calcium hydroxyapatite signal was about 10 gauss and so the measured shift of about 0.2 of a gauss is accurate to about 0.05 gauss. The

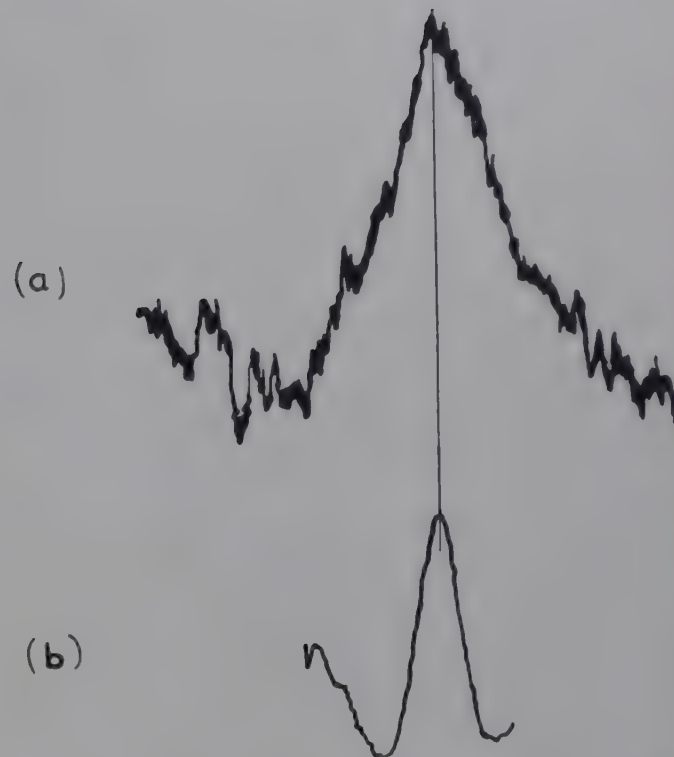


Fig. 2—Wide-Line Nuclear Magnetic Resonance Spectrum of Strontium Hydroxyapatite.

- (a) Spectrum of Strontium Hydroxyapatite
(b) Reference Signal from 85% Phosphoric Acid

proton spectrum from these samples was also examined but signals were found to be very broad.

The infrared spectra of these samples have recently been reported²⁻³.

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Response of *Aman* Paddy and Potato to Soil and Foliar Applications of Various Nitrogenous Fertilizers

By

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Current progress in the formulation of water-soluble high analysis fertilizers and engineering advances in the spraying equipments prompted investigations in the possibilities of foliar applications of nutrients. The present work was undertaken to evaluate the efficiency of foliar fertilization in comparison to soil fertilization. The foliar application of fertilizers proved superior in terms of straw yields of paddy. However, in case of potato no difference was observed between the foliar and soil applications.

Spray fertilization has been drawing attention of the agricultural scientists in recent years. Studies carried out to evaluate the efficiencies and economy of foliar fertilization¹⁻³ indicated considerable promise, followed by reports on greater absorption of added nutrients from the foliage, their active translocation and metabolism⁴⁻⁸. Recent studies also reveal that foliar application of urea attributes to higher yields and better quality of wheat⁹.

Studies so far carried out in India have also strengthened the ground for foliar fertilization for boosting up crop production¹⁰⁻¹¹. The superiority of foliar application over soil application of phosphatics on berseem has been reported¹² whereas the reverse trend has also been noted in case of higher levels of foliar applied nutrients in potato. The findings of Mukherjee¹³ et al are in conformity with the latter observations. They observed that with an increase in the rate of nutrient utilization, efficiency of the foliar applied nutrients decreased.

With this background, the present work was undertaken at the Fertilizers Trial Station, Sindri, in 1965-66 to study the responses of *Aman* paddy (*Patnai* -23) and potato (Royal Kidney) to soil—and foliar applied nitrogenous fertilizers.

Materials and Methods

Plots with uniform nutrient status, drainage and exposure were selected for experimentation (Table 1).

TABLE 1—ANALYSIS OF SOIL SAMPLES
(on Oven-dry basis)

	Aman paddy	Potato
A. Mechanical Analysis, %		
Clay	28.01	23.32
Silt	20.62	24.35
Sand	46.49	47.58
B. Chemical Analysis, %		
Organic carbon	1.003	0.931
Total nitrogen	0.145	0.101
Total P ₂ O ₅	0.158	0.143
Total K ₂ O	0.859	0.823
pH	8.1	7.2

The experimental fields were prepared following standard cultural procedure¹⁴ and laid out in split plots with two replications, the net plot sizes being 1/2000th and 1/4480th of a hectare for paddy and potato respectively.

All the plots received an initial basal dose of phosphorus and potassium at 25 kg. P₂O₅ and 25 kg K₂O/hectare for paddy and 200 kg P₂O₅ and 100 kg K₂O/hectare for potato.

Seedlings of *Aman* paddy were raised on specially prepared seed beds and transplanted at the age of 30 days with a spacing of 23 cm. × 23 cm. Well-sprouted, disease-free potato tubers of uniform size were planted at a distance of 21 cm. in 63 cm. wide rows.

The main treatments consisted soil (S) and foliar (F) applications while the sub-treatments were of various sources of nitrogen viz. (1) urea (U), (2) ammonium bicarbonate (B), and (3) ammonium sulphate (A). Along with these, an additional source of nitrogen i.e., ammonium sulphate nitrate (D) was tried on potato. The various levels of nitrogen and the quantity of fertilizers used under various methods of application are given below (Table 2).

Altogether two soil and six foliar applications were made according to the schedule given in Table 2. The first soil application to *Aman* paddy was made one month after transplanting, while potato received it 40 days after planting. The second soil application was made 4 weeks after the first application in both the cases.

Foliar application was made with half of the total dose, while the remaining half of the nitrogen was top-dressed in between rows on the date of first soil application. Foliar application was made in six equal instalments at weekly intervals, commencing on 3.10.67 and 25.1.68 in paddy and potato respectively. In all the foliar applications the total volume of the spray was kept uniform i.e. 2 litres on each occasion.

The necessary cultural and plant protection measures were taken. Observations on growth characteristics were also noted at regular intervals during the entire growing period together with the final yields.

TABLE 2—FERTILIZER SCHEDULE FOR AMAN PADDY AND POTATO

Forms of Nitrogen	Levels of Nitro- gen, kg./Hectare		Quantity of Ferti- lizer for One Soil Application, g.		Quantity of Fer- tilizer for One Foliar Applica- tion, g.	
	Aman Paddy	Potato	Aman Paddy	Potato	Aman Paddy	Potato
Urea	15	62.5	17.025	52.139	2.837	8.689
	30	125	34.050	104.278	5.674	17.378
	60	250	68.100	208.556	11.348	34.756
Ammonium Bicarbonate	15	62.5	46.875	143.554	7.812	23.925
	30	125	93.750	287.108	15.625	47.850
	60	250	187.500	574.216	31.248	95.700
Ammonium Sulphate	15	62.5	37.500	114.843	6.250	19.140
	30	125	75.000	229.686	12.500	38.280
	60	250	150.000	459.372	25.000	76.560
Ammonium Sulphate Nitrate	—	62.5	—	88.200	—	14.700
	—	125	—	176.400	—	29.400
	—	250	—	352.800	—	58.800

Aman paddy was harvested after 113 days after transplanting and potato 117 days after planting.

Results and Discussion

The data (Table 3) indicated a significant effect of various treatments on the straw yield of paddy except in the case of $M \times F$. The grain yield was, however, affected significantly by the levels of nitrogen only.

TABLE 3—AVERAGE YIELD OF PADDY AND POTATO, Kg./plot

Treat- ments	Average yield					
	Paddy				Potato	
	Straw		Grain		Foliar	Soil
	Foliar	Soil	Foliar	Soil		
U ₁	4.200	5.450	2.785	2.475	4.862	2.987
U ₂	8.350	6.800	2.600	1.805	3.012	3.537
U ₃	10.350	9.450	1.610	1.655	2.850	4.750
B ₁	7.400	6.450	2.715	2.555	3.162	2.900
B ₂	8.550	8.100	2.605	2.325	3.950	4.262
B ₃	9.400	9.600	1.555	1.790	2.312	5.037
A ₁	5.350	6.550	2.820	2.915	3.360	3.175
A ₂	7.700	7.550	2.365	2.725	2.737	3.512
A ₃	8.800	7.900	1.595	1.955	2.475	4.550
D ₁	—	—	—	—	4.550	3.287
D ₂	—	—	—	—	3.337	3.950
D ₃	—	—	—	—	2.437	4.350

F value for

Methods	562.00**	—	—
Fertilizer	125.66**	—	—
Levels	70.72***	54.48**	—
$M \times L$	26.95**	—	155.09**
$F \times L$	22.63***	—	6.86**
$M \times F \times L$	11.47**	—	—

**Significant at 1% levels of significance

***Significant at 0.1% levels of significance

Foliar applications were decidedly superior to soil applications in increasing straw yields, but no such difference was observed in respect of grain yields.

Amongst the nitrogen sources ammonium bicarbonate proved to be the best, while urea and ammonium sulphate followed very closely in increasing the yield of paddy straw. However, the foliar application of urea at 60 kg. N/ha produced higher straw yields than the soil or foliar application of ammonium bicarbonate at equivalent level.

Straw yields increased with increasing levels of nitrogen while grain yields decreased with increase in

levels of nutrient application. The highest grain yield was obtained with soil application of ammonium sulphate at 15 kg. N/ha. level, whereas foliar application of ammonium bicarbonate at 60 kg/ha resulted in lowest yield.

Neither the method of application nor the sources of nitrogen had significant effects on the yield of potato tubers. The yield of tubers increased with increase in the levels of soil application, whereas the reverse trend was observed in foliar application. The highest levels of foliar application of nutrients apparently inhibited the growth and yield, while soil application of nutrients at equivalent rates helped in increasing the number of tubers per plant. No other treatments excepting the interactions, $M \times L$ and $F \times L$ affected the tuber yield.

The best yield responses were obtained from soil application of Ammonium bicarbonate at 250 kg/ha level and the lowest from foliar application of the same at equivalent level.

Summary and Conclusion

The foliar method of application proved superior to soil applications as regards straw yields of paddy, though no such difference was discernible in case of tuber yields of potato.

Among the fertilizers used, ammonium bicarbonate proved superior in encouraging straw yield of paddy, though no significant difference could be obtained in case of tuber yields of potato.

The response of paddy to various levels of applications manifested into an increased straw yield and a decreased grain yield with increasing levels of nitrogen. However, potato responded with increasing tuber yields in case of soil application, while a reverse trend in foliar application was observed.

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Tetraploidy In Pomegranate (*Punica granatum* L)*

By

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A spontaneously occurring tetraploid has been found in pomegranate (*Punica granatum* L). The material showed all characteristic features of tetraploidy in its vegetative as well as reproductive parts. The plant was also found to have a double chromosome complement over diploids. Because of high pollen sterility, even though not useful for immediate direct use, the material is expected to be important genetically for triploidy or tetraploidy breeding.

Bud mutations of "gigas" types have occurred occasionally in various fruit trees like, apple, pear, plum, currants, grape, etc., and they have been found as either wholly teraploids or diploid-tetraploid cytochimeras. Especially in grapes, these "giant" bud sports

have been grown commercially for their larger berries. Besides teraploids, which are being used in breeding experiments, spontaneously occurring triploids resulting from the unreduced gametes have also been of great use in apple cultivation and, in fact, one-third of the commercial apple varieties are triploids.

The present note records for the first time the occurrence of tetraploidy in pomegranate (*Punica granatum*

*This work was carried by the authors elsewhere before joining this Division of FCI Ltd.

L). in the variety G. B.—1. The material in which tetraploidy has been detected was received as a clonal material (air layers) from the Government Horticultural Research Station, Poona. In the course of observation of growth data and other morphological characteristics of radiation effect, one plant appeared somewhat different in appearance from the rest of the stock. On close study, it showed having slightly bigger and thicker leaves. The plant was also found to differ from others in not having fruiting in spite of profuse number of

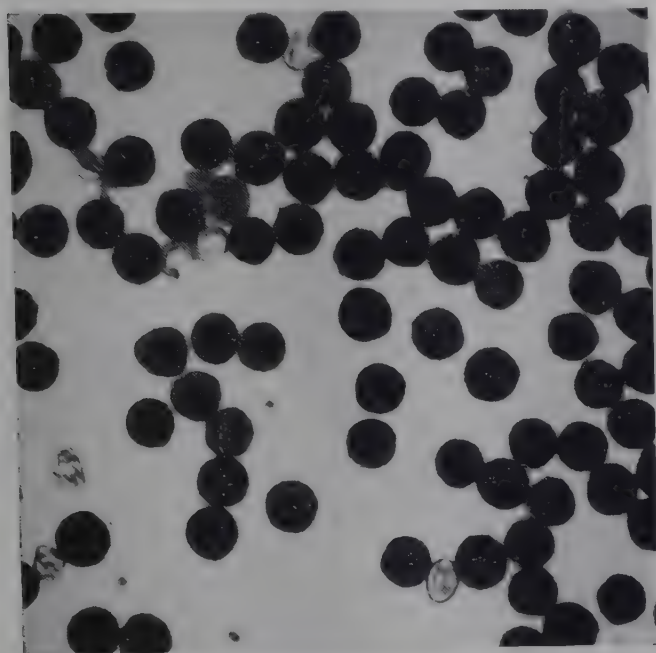


Fig. 1—Showing High Degree of Pollen Fertility in Diploid. ($\times 300$)

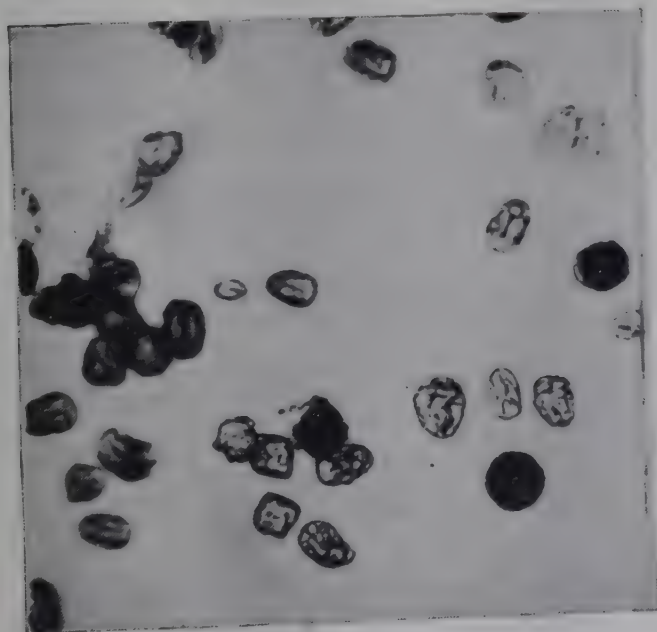


Fig. 2—Showing High Degree of Pollen Sterility in Tetraploid. ($\times 300$)

hermaphrodite flowers. When the pollen fertility was checked by acetocarmine stainability test, it was found mostly with sterile pollen grains (Figs. 1 & 2). Flower buds were fixed in propino carnoy, saturated with ferric chloride and stained with acetocarmine for meiotic studies and it was observed with a chromosome complement of $2n=32$.

Even though detailed cytological analysis was not performed, mostly bivalents and few univalents were recorded in Metaphase I and in Anaphase I & II generally a regular separation of 16 chromosomes was noticed (Fig. 3). Although some erroneous reports have appeared early on the cytology of pomegranate, later on all workers confirmed its chromosome number as $2n=16$. Nath and Randhawa¹ also worked out the cytology of six important Indian pomegranate varieties including the present one, G.B. —1 and observed 16 as the somatic number in all, except the variety Double Flower (an ornamental type) which, however, has $2n=18$.

A comparative study of diploid and tetraploid plants revealed that both the size and shape of leaves changed due to tetraploidy. The average size of 4th leaf (from the top) in tetraploid measured 8.54 cm^2 as against 8.01 cm^2 in diploid and the corresponding figures for 8th leaf were 10.89 cm^2 and 10.01 cm^2 . The leaves in tetraploid were broader i.e. greater W/L (width/length) ratio than those of diploid. Though the frequency of stomata (in unit microscopic field) decreased due to tetraploidy

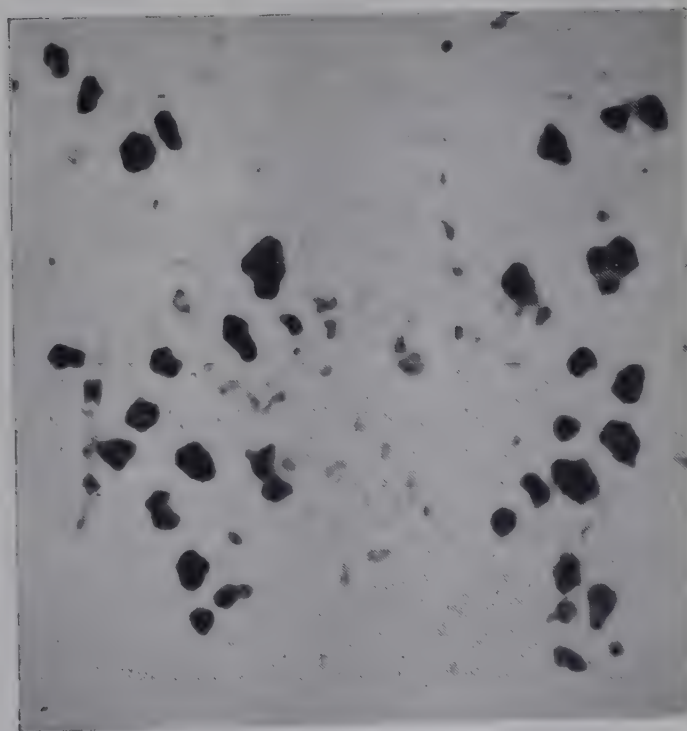


Fig. 3—Anaphase I, Showing Normal Separation of 16 Chromosomes in each Pole. ($\times 1500$)

(45.6 in tetraploid, 48.7 in diploid), the size of stomata as indicated by the length and breadth of guard cells increased due to tetraploidy. The average length and breadth of guard cells in tetraploid was recorded 19.22 microns and 6.12 microns against 18.72 microns and 5.88 microns in diploids. The pollen grains of tetraploid were also found to be bigger but with a high degree of sterility. The size of pollen grains in tetraploid was 32.4 microns as compared to 21.6 microns in diploids but the pollen sterility was 85.4 per cent in tetraploids and 7.4 per cent in diploids. These distinctive characters i.e. bigger leaves, stomata, pollen grains and high sterility are common in tetraploid materials. Moreover, they are slow-growing with coarser leaves and have bigger plant parts including flowers and fruits.

Though the plant in the present case has been spotted out under chronic gamma irradiation condition, the change is not a radiation-induced one, because, at the time of detection, the plant received only a meagre dose of 630 R (1.2 R/hr.). Moreover, the full-grown plant at the time of isolation was having all the branches at different stages of growth with ploidy characteristics. This indicated a spontaneous change at an early stage of plant establishment. The material is, however, under observation so as to study its possibility as a breeding material.

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Estimation of Urea by Polarographic Method

By

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Urea has been found to affect the limiting current of Ti^{4+} in 0.4 N sulphuric acid and 0.3 M ammonium sulphate base electrolyte. The plot of i_d against concentration of urea in this solution is found to be linear which is utilized for the estimation of urea polarographically.

Introduction

In a urea plant, quick estimation of urea is important in process streams and recycle liquors. The standard method¹ of estimation by Kjeldahl digestion is not suited for routine analyses. The urease method of Fox and Geldard² later adopted by Association of Official Agricultural Chemists³ is time-consuming and has other limitations. It was thought desirable to evolve a quick method for the estimation of urea.

Experimental

Polarograms were recorded on LP-60 (KOVO Instrument CO., Czechoslovakia) self-recording polarograph with dropping mercury electrode. The glass capillary with $m^{2/3} t^{1/6} = 4.07$ at the $h = 33.7$ cm was used. All studies were carried out in a H-type cell. Nitrogen was bubbled, before each experiment to effect

deaeration. All polarographic studies were carried out at 30°C. Stock solution of titanium was prepared from A.R. potassium titanyl oxalate as given by Vogel⁴.

Calibration of Working Graph

In a series of 100 ml. volumetric flasks, calculated quantities of titanium solution, sulphuric acid and ammonium sulphate and urea ranging from 0 to 1.75 gm were added. The solution after diluting to mark had Ti^{4+} 0.005 M, sulphuric acid 0.4 N, ammonium sulphate 0.3 M and different amounts of urea. Polarogram of each solution was recorded. Diffusion currents were calculated (Table 1) and plotted against urea concentration.

The following procedure is adopted in the estimation of urea in an unknown sample.

A weighed quantity of the sample, either in the solid form or in aqueous solution was taken in a 100 ml volumetric flask so that the quantity of urea present did not exceed 1.5 g. Measured volumes of stock solutions of Ti^{4+} , sulphuric acid and ammonium sulphate were added so that after dilution the solution contained Ti^{4+} .005 M, sulphuric acid 0.4N and ammonium sulphate 0.3 M. The polarogram was recorded, diffusion current was calculated and urea content was found out from the calibration curve. The results of various analyses are given in Table 2.

Discussion

A well defined wave with $E_{1/2}$ vs SCE = 0.26 volts is obtained for Ti^{4+} in base electrolyte consisting of 0.4 N sulphuric acid and 0.3 M ammonium sulphate. The slope of E_{de} vs $\log i/i_d - i$ plot was found to be 0.059, confirming that the system is reversible with one electron reduction of Ti^{4+} . Urea was found to affect the limiting current as well as $E_{1/2}$ of Ti^{4+} in the above-mentioned electrolyte. The results are presented in Table 1. The plot of urea concentration against diffusion current was found to be linear upto 0.30 M urea and this working graph was used to determine urea polarographically.

The values of $E_{1/2}$ was shifted to more negative potential. This is attributed to the formation of a titanium-urea complex. Further work is in progress and will be published in a subsequent communication.

In Table 2 are given results of estimations of various samples containing urea. The individual errors in the samples were calculated to be within 2 per cent and are given in the last column of Table 2.

The polarographic method of estimation of urea developed in this laboratory gives a quick and reasonably accurate result within half an hour and can be applied to samples both in the solid and solution form.

TABLE 1—EFFECT OF UREA CONCENTRATION ON THE VALUE OF i_d AND $E_{1/2}$ OF Ti^{4+} BASE ELECTROLYTE

		H_2SO_4	— 0.4 N
		$(NH_4)_2 SO_4$	— 0.3 N
		Ti^{4+}	— 0.005 N
Amount of Urea/ 100 ml., g.	Concentration of Urea in moles	$E_{1/2}$ Vs S.C.E. volts	i_d Diffusion Current, m.a.
0.0	0.00	0.260	0.45
0.25	0.042	0.275	1.00
0.50	0.083	0.290	1.45
0.75	0.125	0.305	1.90
1.00	0.166	0.315	2.32
1.25	0.208	0.325	2.90
1.50	0.250	0.330	3.35
1.75	0.291	0.335	3.90

TABLE 2—POLAROGRAPHIC DETERMINATION OF UREA BASE ELECTROLYTE

	H_2SO_4	— 0.4 N
	$(NH_4)_2 SO_4$	— 0.3 N
	Ti^{4+}	— 0.005 N

Sample	Urea Added, i_d , micro-amp. g.	Urea found Polarographically, g.	% Error
1.	0.360	1.20	0.0
2.	0.806	2.10	— 0.74
3.	0.863	2.21	+ 0.81
4.	0.609	1.70	+ 0.02
5.	1.051	2.45	— 2.00
6.	0.954	2.35	— 1.50
7.	0.275	1.05	+ 1.80
8.	0.934	2.30	— 0.81
9.	0.727	1.95	+ 1.80
10.	1.225	2.90	+ 0.40

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Nuclear Desalination of Sea Water and Fertilizer Manufacture

By

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Explaining the current single- and dual-purpose fuel and reactor technology in desalting sea water, this paper compares the advantages and disadvantages of the two processes in particular reference to Bombay's power and water supply. The studies carried out by Burn & Roe of New York for a 100 mgd plant, (single-purpose) and Kaiser Engineers for a 100 mgd dual-purpose plant 150 mgd by Bechtel and Grace process for by-product fertilizer recovery plant have been extensively quoted for the purposes of costing, running expenditure and annual revenue, etc. Unlike other countries, today India needs fertilizers for food self-sufficiency and has proposed to put up additional fertilizer plants to the tune of Rs. 335 crores, with a foreign exchange component of Rs. 135 crores, and, in addition, is proposing to import fertilizers to the tune of Rs. 259 crores. Thus, the 4th Five Year plan provides Rs. 594 crores with a foreign exchange component of Rs. 394 crores. The cost of a triple-purpose plant—which is India's need today—for water, power and fertilizer is estimated at Rs. 350 crores with an annual cost of Rs. 146.60 crores, an annual income of Rs. 151.80 crores and is a *prime facie* case of economic feasibility. Technical feasibility is already established by the above-mentioned three renowned consulting engineers' firms.

At present Bombay is supplied 220 mgd water from *Tansa*, *Tulsi* and *Vaitarna* through over 70 miles surface-laid 6-9' diameter steel mains—crucial point being Kassuli bridge—over which all these pipes pass. Power is supplied from *Koyana*. In the context of present-day international situation, it is essential to provide independent source of water for Bombay, which would also meet the vagaries of monsoons apart from defence reasons.

Recent advances ¹⁻⁵ in nuclear desalination of sea-water with multistage flash evaporators ⁶⁻⁸ by dual-purpose reactors have made this process as economical as bringing water from a distance which would in addition provide power and potential requirement of chemical fertilizers. It is known that India is spending about Rs. 335 crores for putting up additional fertilizer plants with a foreign exchange component of Rs. 135 crores (before devaluation) and it is also proposed to import fertilizers of the value of Rs. 259 crores (before devaluation). In fact, the Fourth Plan provides Rs. 594 crores for fertilizers with a foreign exchange component of Rs. 394 crores. Therefore, the examination of the econo-

mics of desalination of sea water in the context of supply of fresh water and power and the recovery of by-product fertilizer and other chemicals seems feasible for the development of this process in the coastal cities, like Bombay, Madras, etc., in India.

Types of Nuclear Desalination Plants

There are two types of nuclear-powered desalting plants, viz. (1) single-purpose plants for the production of water, and (2) dual-purpose plants for the production of both water and power for sale.

Single-Purpose Plants: In this process, the full steam-flow required for the water plant is first used for power generation in a topping back-pressure turbine generator. It is believed⁹ that the large single-purpose reactor pow-

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ered water plants (Table 1), with their independence of power generation, may find a broader market and a more ready application than the dual-purpose plants, because (a) arid and semi-arid regions need much water but little power; (b) water and/or power transmission costs raise dual-purpose plant costs; (c) dual-purpose plants cannot give high efficiency when they follow demand; (d) water-purpose plants produce large blocks of power; (e) single-purpose plants produce efficiently where only water is needed; and (f) lower capital investment fills the need for water.

Dual-Purpose Plants: The economics are certainly attractive in this case, since the capital and operating costs can be distributed between power and water, thereby permitting lower production costs for either or both products (Fig.2). Yet such plants have a number of restrictions which can penalize production costs and limit this flexibility of operation. A dual-purpose plant designed to meet large water demands will generate a large block of power. However, most of the arid and semi-arid regions in the world are not industrialized sufficiently to use the power. In areas requiring both power and water, dual-purpose plants with 10 mgd capacities can be economical if they are designed for fixed—rather than flexible—product ratio and tailored

to a particular application. It costs very little more in nuclear boilers to generate steam at 540°F than at the 250°F, which a conventional sea water distillation plant can currently use. When both products, viz. water and power, are considered together, the combined facility can utilize heat as efficiently as a single purpose power plant operating over the same temperature range, while this neither lowers nor raises the cost of the steam to the water plant, and is radically lower than if the steam were generated for direct utilization in the water plant.

The dual-purpose plant offers other advantages, the main advantage being the decreasing unit cost of the nuclear steam-generating equipment with increasing size. Since the combined facility calls for a steam supply,

TABLE 1—EQUIPMENT DESIGN FEATURES OF NUCLEAR-FUELLED CONTROLLED FLASH EVAPORATION DESALTING PLANT*

Reactor Plant	
Thermal power (Mw)	2,130
Fuel	{ A1-Clad U-nat
Burn up (avg Mwd/tonne U)	6,000
Core inventory (kg UO ₂)	142,000
Vessel diameter (ft)	37
Vessel thickness (inch)	2.5
Vessel material	A1
Core height and diameter (ft)	22
D ₂ O core inlet temp (°F)	185
D ₂ O core outlet temp (°F)	235
Total D ₂ O flow (10 ³ gpm)	72.8
Primary pumps (Nos.)	4
D ₂ O inventory (106 lb)	1.33
D ₂ O loss (lb/yr)	26,000
Water Plant	
Vessels (Nos.)	28
Vertical stages/vessel (Nos.)	10
Brine heaters (Nos.)	14
Heat transfer surface/heater (ft. 2)	63,500
Performance ratio (lbs. of water/1000 Btu)	4.76
Vessel height (ft)	40
Vessel width (ft)	20
Vessel length (ft)	47

*Capacity 100 mgd

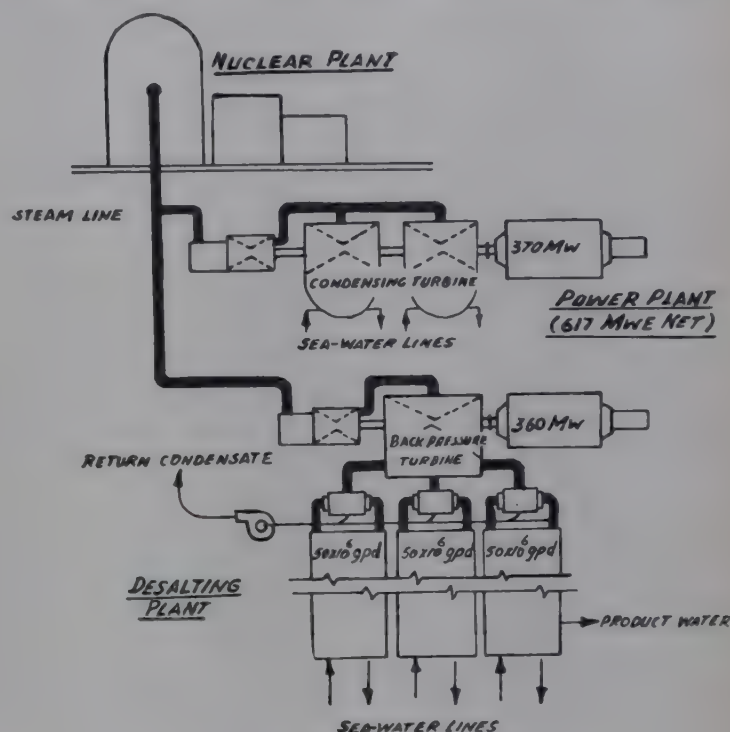


Fig. 1—Dual Purpose Nuclear Plant.

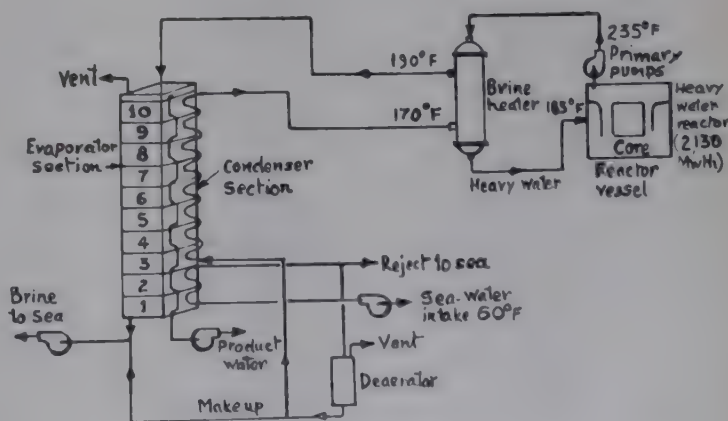


Fig. 2—Controlled Flash Evaporator Units for a Single Purpose Desalting Plant of 100×10³ gpd Capacity. (Evaporators are in Vertical Stages)

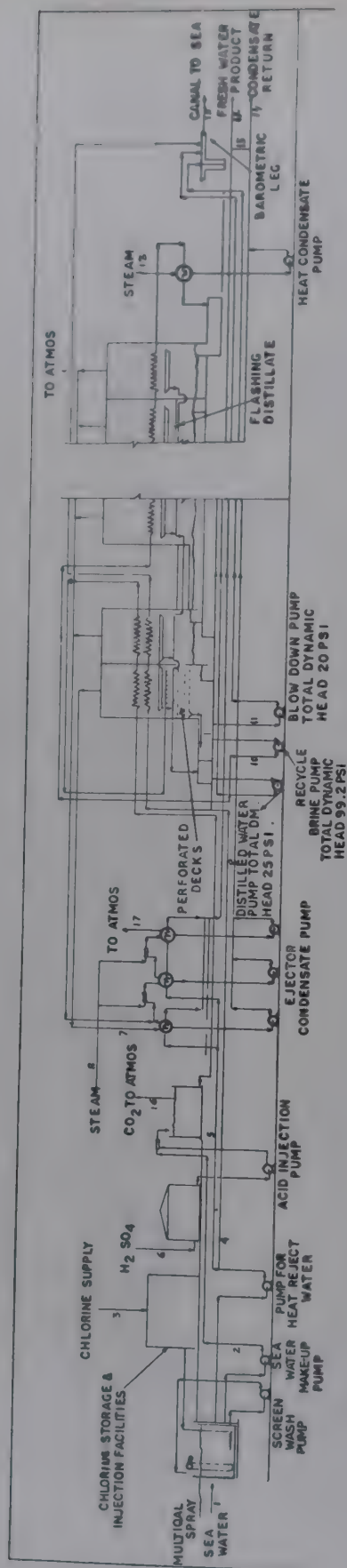


Fig. 3—Kaiser-CCC Dual Purpose Plant (flowsheet)

Legend

Components	Stream No.	1	2	3	4	5	6	7	8	9
Flow (LB/HR)		268,800,000	69,500,000	40	211,000,000	8,300,000	9,650	63,500	110,000	157,000
Flow (GPM)		562,000	135,000		411,000	16,000				314
Temperature (F°)		70	70	70	70	70		80	365	120
Pressure (PSIA)		—	—	—	—	—	—	1"Hg	165	
Dissolved Solids (% by wt)		3.86	3.86	3.86	3.86	3.86				
Non-Condensable (% by wt)								25		

	10	11	12	13	14	15	16	17	18
Flow (LB/HR)	290,000,000	34,750,000	34,750,000	3,400,000	3,560,000	254,100,000	7,800	16,500	47,000
Flow (GPM)	550,000	66,000	69,500		7,100	493,000			94
Temperature (F°)	82	82	80	240	236	82	70	105	120
Pressure (PSIA)				25					
Dissolved Solids (% by wt)	6.8	7.72				4.3			
Non-Condensable (% by wt)								96	

then either power generation or a distillation plant with the same capacity, associated unit costs for both capital and fuel can be markedly lower. Other advantages are either partial or complete elimination of the condenser (by virtue of the brine heater) and secondary water system and the economy of operating both plants under a common staff.

The dual-purpose plant has a certain degree of flexibility in selecting the *water-to-power ratio*, which can be used advantageously in determining the temperature of the steam going to the water plant. Although the maximum temperature is currently limited because of scaling and corrosion consideration to about 250°F, lower ratios can be achieved with lower temperature steam at little or no penalty to the cost of either product. But flexibility in operation is another matter. The electrical energy must be used as it is generated, whereas water can be stored: this has given rise to the argument that the *ratio of power to water* in a combined plant should be varied to match the daily and perhaps seasonal load variation of the electrical system.

However, this imposes an economic penalty, since the varying of the ratio displaces the operation from the economic optimum for which it was designed, i.e. the plant should be base loaded for both power and water. Thus, the best use of the total capital investment is obtained when the plant factor is a maximum for both products, which precludes the use of wide swings in output. Other means for generating power at a lower capital cost should be provided to handle the power peaks.

Typical Desalting Installations

Single-Purpose Plant: A 100 mgd single-purpose plant (Fig.2) designed by Burns & Roe, Inc., New York⁹, is based on four loops with a single pump for each loop. Vertical pumps are mounted on the reactor for the primary heavy water circulating system and are arranged so as to recirculate all the heavy water leakages at pump scale into the reactor. Adjacent to the desalting vessels, the brine heaters are located. The lengths of heaters were selected to permit tube-bundle withdrawal for access and repair. The reactor vessel design is based on an aluminium alloy stainless steel with thermal shields—cooled by heavy water in the reflection section—located within it to reduce the radiation damage in the wall. Facility for personal access is provided to the contaminant area through an underground passage below another section of the evaporator container. The auxiliary system, such as deuterium and oxygen recombiners, a by-pass ion-exchange clean-up system, a heavy water

deuterium make-up system and a helium system for reactor vessel blanket, are located below the reactor operating level adjacent to the reactor.

Dual-Purpose Plant: A 100 mgd dual-purpose plant designed by Kaiser Engineers¹¹ for desalting sea water and production of 175-200 Mwe net saleable power is the non-conventional man-made water resource for Israel's water demands after 1970. The process selected utilizes the multistage flash type evaporators, arranged in four parallel discrete trains each with a capacity of 25 mgd (Fig.3) and each train is subdivided into four parallel streams, for 6.25 mgd each, separated by walls. The trains can be operated independently of the others, but it is not possible to operate or shut-off one stream within a train. The body material of the evaporator is concrete.

Energy for the desalting plant is supplied from steam condensing in the brine heater after it has expanded through a turbine to produce the specified net saleable power and the power required for the heat source, power plant, and water plant auxiliaries. Each evaporator train consists of a recovery and a heat reject section, brine heater, pumps and vacuum system (Fig.4). The brine channel extends the full width of the flow in each sub-train (Module) and carries the brine flow in parallel to the tube bundle. The condensate is collected and conveyed through the troughs located beneath the bundles. The inner surface of concrete structure will be lined with a suitable protective material like cement epoxy or epoxy tar. The high temperature stages may warrant a thin metallic lining. The outer surface of the evaporator train will be coated with suitable material to minimize the effect of temperature cycles on the concrete structures.

A 150 mgd desalted water power (750 Mwe) plant, for the metropolitan water district of Southern California, has been designed by Bechtel Corp.¹² The Metropolitan Water District has considered the following points in salt water conversion which are equally applicable to Bombay, Calcutta and Madras water supply: (1) If the economic feasibility study results should be favourable in regard to a desalting plant based on present day technology, MWD would consider undertaking its construction; (2) if there is any interruption of service from present water resources, an auxiliary source would be of great value; (3) the area served by MWD is now supplied with imported water through two long aqueducts from Colorado river and a third will supply water from a still remote area. Each of three aqueducts crosses the San Andreas Fault (one of the major earthquake faults) and other rifts of various

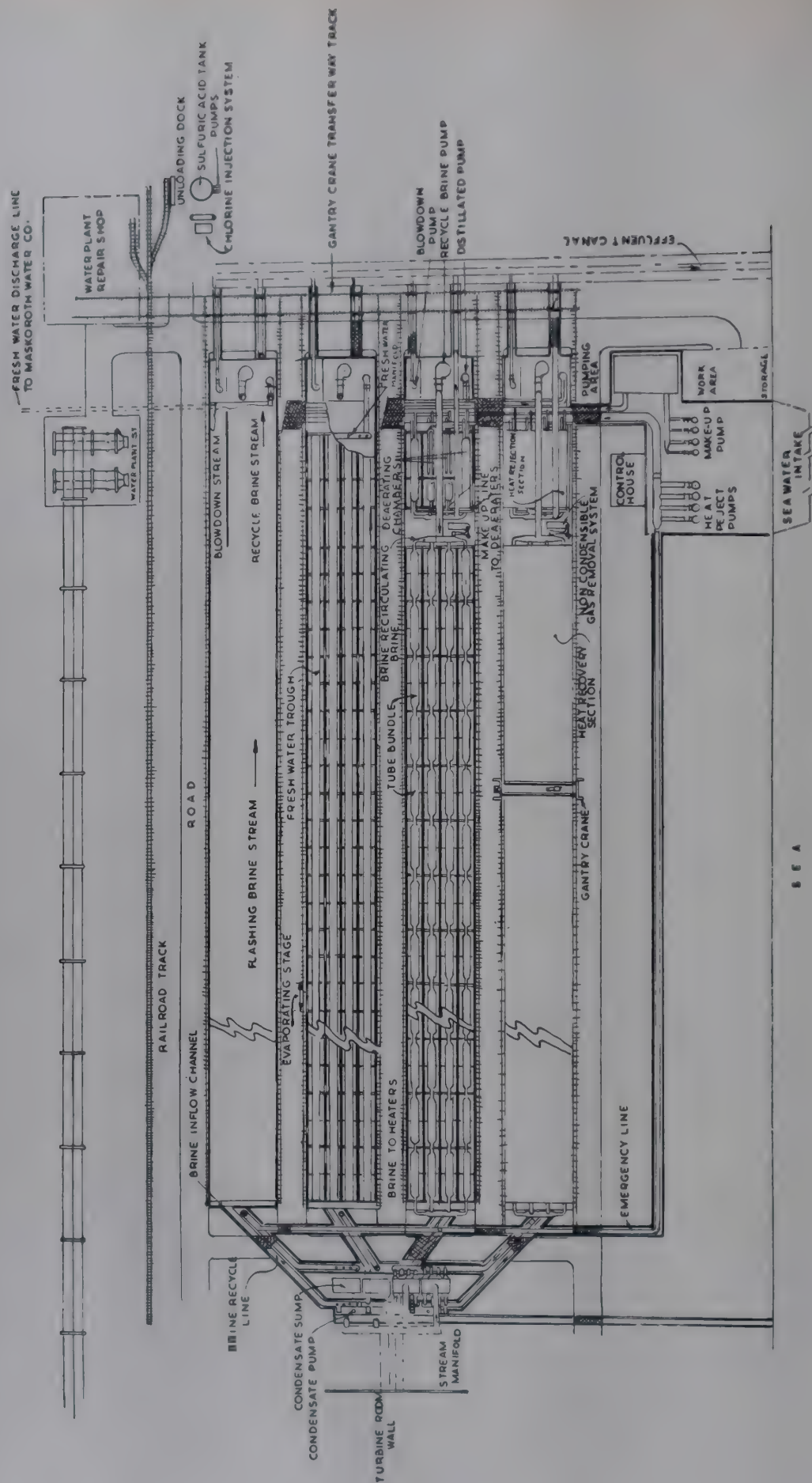


Fig. 4—Details of the Stage.

degrees of potential activity. An earthquake of great magnitude could interrupt services of any one or all the three aqueducts. During this stage the need for an emergency water supply such as desalting plant would be critical; (4) operation of a high capacity desalting plant for an extended period would provide dependable data of extreme value in evaluating various regional plants for augmenting the water and power supply.

The conceptual design layouts after having compared between five power plants and two 150 mgd desalting plants at S. California incorporates 2 nuclear reactors, 3 turbine generators, and a desalting plant composing three parallel plants of 50 mgd capacity each (Fig.5).

Desalting Plant

Sea water, intermittently chlorinated to prevent the growth of marine life, is used as coolant in the condenser tubes of the evaporators heat rejection section. Most of it is then returned to the ocean (Fig.5). The remainder, which is used as feed to the evaporators, enters the deaerator section, where it mixes with recycling brine leaving the last heat rejection stage. The two streams are at essentially the same temperature when mixed.

A quantity of flashing brine, equal to half of the make-up, is rejected to the sea while the rest is recirculated. The balance of the net make-up is accounted for by-product water. A scale-prevention chemical is added to the recycle brine stream as it leaves the vacuum sump. Although the chemical additive is used to control scale, provision is also made for acid addition for scale control and flexibility of operation, should this method prove desirable.

Brine from the vacuum sump below the deaerator is recycled through the recovery section condenser tubes and through the brine heater at a rate of about 9 times the production rate. After being heated to 200°F with 13.3 psia steam from the back-pressure turbine, the brine flows into the first stage of the evaporator to begin a series of flashings. The flowing stream takes its pressure drops from stage to stage through orifices properly sized for each stage. From the final stage, it returns to the vacuum sump.

Distilled product water is collected in open trays under the tube bundles within the evaporator. The distillate flashes from stage to stage as a means of recovering sensible heat; its temperature in each stage will be lower than that flashing brine by the boiling point elevation, the demister loss, and by any superheat in the brine, a total difference of about 2.5°F. The distillate leaves the last stages of heat recovery and rejection at a temperature of about 81°F and drains to a product sump. Due to the low temperature of sea water at site, product water leaving the heat recovery section is removed from the cycle at this point. Product water from the heat rejection stages is collected separately and mixed with the warmer product water obtained from the heat recovery section.

Fertilizer By-Product Recovery in Nuclear Desalination Process

Scale prevention is one of the main challenges in treating sea water. The by-products, such as fertilizer, chemicals, etc. are recovered from the removal of scale formers in this process. The formation of scale on heat-

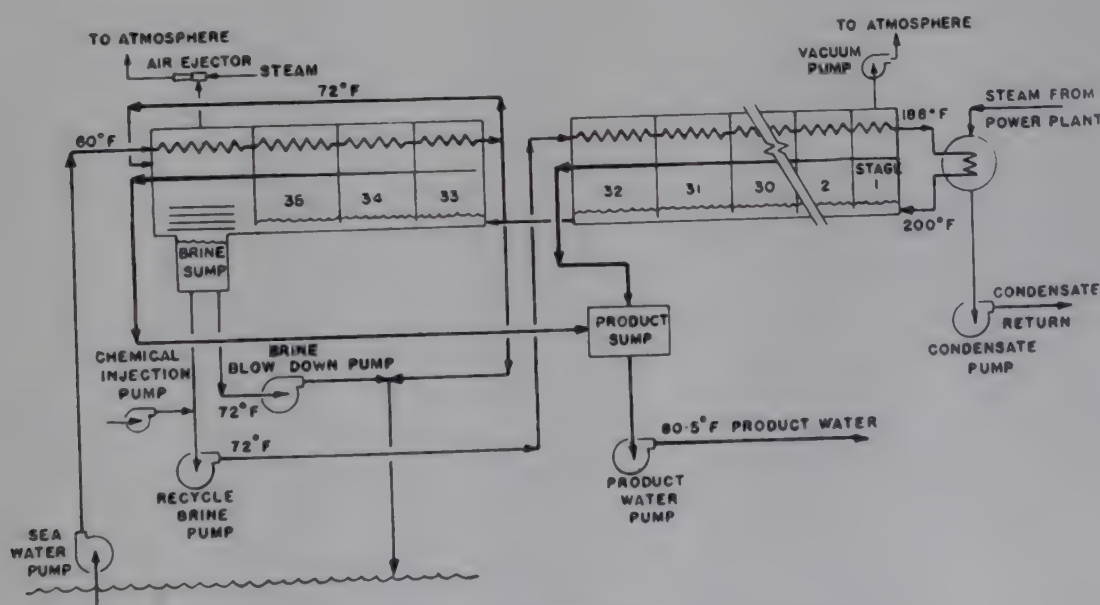


Fig. 5—Simplified Flow Diagram Task Force Desalting Plant.

transfer surfaces reduces greatly the efficiency of the distillation equipment used for the production of fresh water. The scale which is deposited from heated sea water is primarily a mixture of calcium and magnesium compounds, particularly calcium carbonate, magnesium hydroxide and calcium sulphate. To avoid scale formation, distillation equipment has often been operated at lower temperatures (190-210°F) than the optimum. For preventing the formation of calcium carbonate and magnesium hydroxide, temperatures upto 270°F are maintained; while above this acid treatment together with the removal of calcium prior to desalination are necessary. Sometimes small amounts of polyphosphates were added to help complex the calcium and magnesium.

Pretreatment adds to the cost of production which can be neutralized if a by-product is produced simultaneously. A pretreatment process¹³⁻¹⁵ known as *Grace process* which produces a by-product consisting of magnesium, ammonium phosphate and other phosphates for use in the manufacture of fertilizers, has promise for fulfilling these requirements (Fig.6).

Phosphoric acid is added to the sea water and then sufficient ammonia to produce a slurry of pH 8.50. The mixture of precipitated phosphates and sea water is discharged to a settler. After the phosphates have settled, the clear overflow is pumped to the saline water conversion plant. The phosphate slurry (underflow from the settler) is pumped to the dehydrator and maintained at 195°F for one hour.

It is then filtered and the resulting solids are sent to a fertilizer plant where they are mixed with potash and other fertilizer materials, and then granulated, dried, screened and finally bagged. In the dehydrator the phos-

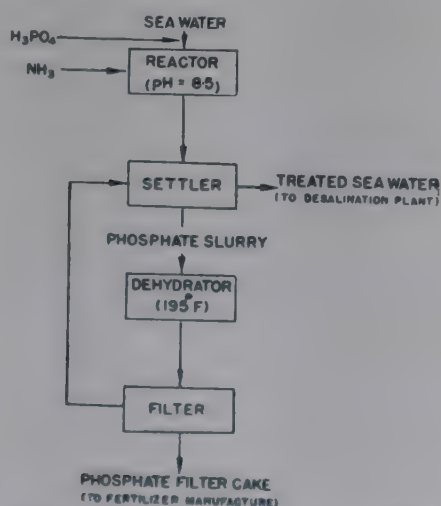


Fig. 6—Removal of Scale Formers from Sea Water by Phosphate Precipitation.
(Simplified Process Flowsheet)

phate slurry is digested at a high temperature (195°F) to convert magnesium and ammonium phosphate hexahydrate to the monohydrate.

The sea water treated in a bench scale model¹⁶, contained 0.3-0.4 ppm of magnesium and 10-11 ppm of calcium (Table 2). Their original contents in sea water are 1132 and 356 ppm and the percentage reductions obtained are 99.6 per cent and 97 per cent respectively. The residual concentration of P_2O_5 in the descaled sea water was 66 ppm which corresponds to a phosphate recovery in the fertilizer product of 98.5 per cent.

TABLE 2—COMPOSITION OF SEA WATER, wt %

Compounds	Water of			
	Ocean	Medi- terranean sea	Bay of Bengal	Arabian Sea
NaCl	2.723	3.007	2.280	3.238
MgCl ₂	0.334	0.385	0.280	0.478
MgSO ₄	0.225	0.249	0.190	0.261
CaSO ₄	0.126	0.140	0.107	0.164
KCl	0.077	0.086	0.057	—
MgBr ₂	0.008	0.008	—	—
CaCO ₃	0.012	0.012	0.011	0.011
Total	3.505	3.887	2.925	4.152

Composition of Filter Cake: The dried filter cake was found to have the following constituents (%by weight): N 7.3, P_2O_5 43.0, MgO 21.0, CaO 5.3 and Moisture 1.4 at 100°C.

With efficient filtration, the chloride content in the dried unwashed solids was brought as low 0.2-0.3 per cent, approximately every 1000 gallons of sea water produces 74 lbs of phosphates.

The distillation of the sea water in a pilot plant (Fig.7) after the removal of scale formers indicated that the problem with scale-formation has probably been eliminated. The presence of ammonia in a significant concentration in the distillate could be eliminated by efficient deaeration of the sea water prior to distillation, but the low pH and hence the corrosive action of distillate needs the necessary rectification on steel, etc. in the unit.

By-product Evaluation

Composition of By-product: The analysis of phosphate granules is shown in Table 3. Dried filter cakes containing 8 per cent nitrogen and 45 per cent P_2O_5 were obtained by the pilot plant. Theoretically, pure

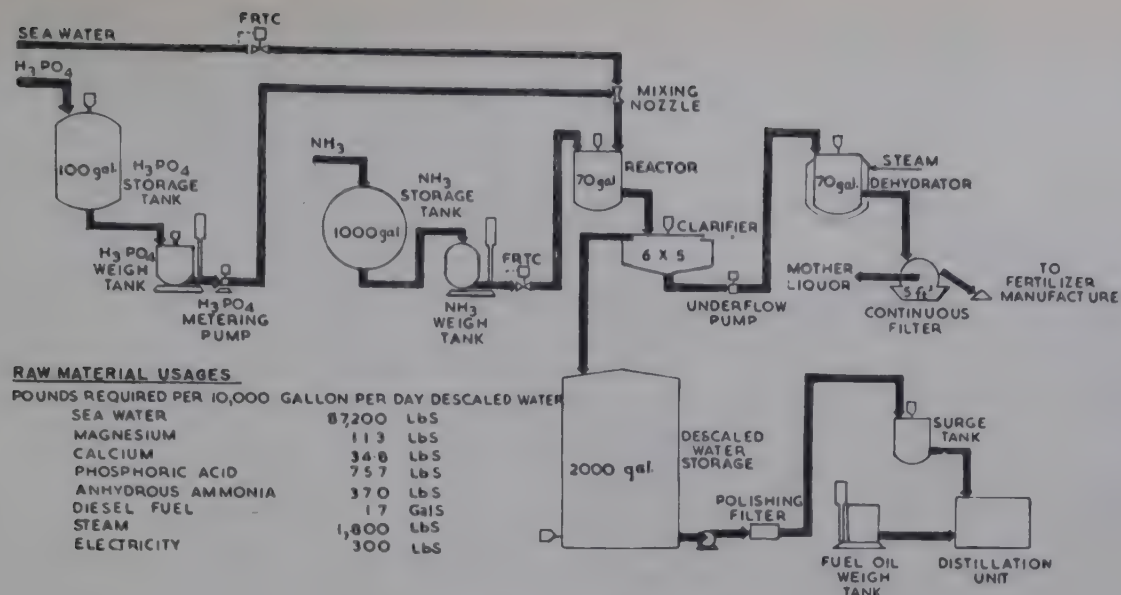


Fig 7—Grace Process for Descaling Sea Water.

magnesium ammonium phosphate monohydrate contains 9 per cent nitrogen and 45 per cent P_2O_5 .

The very low percentage of water-soluble nitrogen (less than 0.05 per cent) is significant. When magnesium ammonium phosphate is produced commercially from conventional raw materials, it contains 1-2 per cent water-soluble and 6-7 per cent water-insoluble nitrogen. Although both materials contain the same total amount of nitrogen (8 per cent), the water-insoluble nitrogen is more valuable.

TABLE 3—COMPOSITION OF PHOSPHATE BY-PRODUCT

	Percentage
Moisture at 100°C	0.42
N	8.00
P_2O_5	45.20
Insoluble P_2O_5	4.08
Avail. P_2O_5 **	41.12
Water soluble N	0.05
MgO	23.39
CaO	5.31

**The percentage of P_2O_5 which is available as a plant nutrient.

Emphasis should be given for high phosphate recovery because the raw material cost for phosphoric acid amounts to more than half the total cost of the process. The amount of H_3PO_5 acid is added stoichiometrically equivalent to the calcium and magnesium in sea water based on the formation of magnesium ammonium phosphate and dicalcium phosphate. An assured recovery of 90 per cent may be reasonably anticipated. When phosphate recovery is improved by operating with less than

the stoichiometric amount of phosphoric acid, the calcium level in treated sea water increases. If treated sea water with 56 ppm of residual calcium is adequate for evaporator feed, significant savings in by-product cost could be achieved due to higher phosphate recovery.

Ammonia Recovery: The maximum amount of ammonia that could be recovered in the precipitate is approximately 28 per cent of the total and the remaining is left in the treated sea water as ammonium chloride (or sulphate). However, it is not lost since most of it can be recovered and recycled.

Agronomic Value: The agronomic properties of magnesium ammonium phosphate are quite remarkable. Because of its low solubility in granulated form it is a slow release fertilizer^{17,18}. It does not leach from sandy or porous solids and will not burn plants even when used in large quantities. Agronomic tests reveal that plants utilize the nutrients from magnesium ammonium phosphate more efficiently than from most conventional fertilizer¹⁹⁻²¹.

The economy of the plant can be obtained much depending on the low raw material costs by: (a) producing at the site, dilute phosphoric acid directly in sea water; and (b) the recovery and recycle of ammonia from the residue brine evaporator.

A fertilizer by-product recovery plant having 15 mgd capacity has been worked out by Th. Messing of Germany. Table 4 shows the capital and manufacturing costs for removing scale formers with by-product recovery.

Recovery of High Purity 'Sodium Chloride': It has been reported recently that the potable water from sea

TABLE 4—CAPITAL AND MANUFACTURING COSTS FOR REMOVING SCALE-FORMERS WITH BY-PRODUCT RECOVERY (15 mgd Plant)

<i>Basis:</i>	
Sea Water Treated (gallons/day)	15,000,000
Fresh Water Production (gallons/day)	10,000,000
Brine Concentration Factor	3 : 1
Fertilizer Production (8-45-0) dry basis (tons/day)	590
Location	Florida
<i>Total Plant Investment</i>	
Sulfuric Acid	\$ 1,900,000
Phosphoric Acid	\$ 1,900,000
Ammonia Stripping	\$ 2,600,000
Chemical Treatment	\$ 4,200,000
TOTAL (not including distillation)	\$ 10,600,000
<i>Manufacturing Costs</i>	
Fertilizer By-Product	\$ 54.20
Treated Sea Water	\$ 0

water can be combined with the recovery of high purity sodium chloride. Feasibility study of such proposals already carried out in Arabia, Pakistan, and India²², indicated that there are no technical difficulties. Such plants can produce potable water and pure evaporated salt on an economic cost basis.

Cost Analysis and Capital Investment of Typical Plants:

It is reported that the water costs of a single-purpose plant is little higher than that could be obtained from the dual-purpose plant. The study on the dual-purpose plant of size 100 mgd showed the water cost in the range of 31-34 cents per 1000 gallons. An additional amount of 10 cents per 1000 gallons is accounted for in single-purpose plants. From the nuclear desalting study in Israel which does not include any other by-product recovery, the following values are obtained as the unit water costs at different fixed charge rates for the optimized selected plant (100 mgd and 200 Mwe) at plant site; water costs (per 1000 gals.) are 25.20, 36.70, and 55.50 cents for 5, 7 and 10 per cent fixed charge rates respectively.

There are many variables, like reactor size, transmission costs, etc., that affect cost of water in a desalination plant. When a reactor is considered in a range of 25000 Mwth the cost of energy produced is attractive not only because of fuel cost reductions per kW of rating, but also of great economics achieved in fuel costs per unit energy from mass production of fuel and the lower depletion and use charges per unit energy. However, largescale reactors are more dangerous and requires siting places far away from populated areas; this requirement obviously counters the production economy with

increasing power and water transmission costs. This is the case also with the dual-purpose plants at places of arid and semi-arid regions which are not industrialized sufficiently to use the power. It is possible that even the industrialized places may not be able to use the power.

Transmission Costs: A dual-purpose plant, from which water is pumped 40 miles, will have an additional water production cost of 6-12 cents per 1000 gals²³. High voltage power transmission increases production costs by 0.2 cents-kW-hr for a distance of 100 miles²⁴. Dual-purpose studies have indicated water production costs of 20-40 cents per 1000 gals for plants greater than 50 mgd.

Size Scale-up Factor: Though the size scale-up lowers unit costs, it is not realistic to consider plants larger than those that can be utilized in the existing systems. The economy of largescale desalting plants is obvious when the variation of unit cost with capacity, and the lower-cost alternative means of supplying water are examined thoroughly. The traditional method for water deficient areas is usually to transport water from distant sources by pipelines or aqueducts. On a general basis, when transportation on unit distance basis²² and nuclear desalting²⁴ costs are compared as a function of capacity (Figs. 8 and 9), apparently water transportation costs vary inversely as the square root of capacity, whereas the scaling law for nuclear desalting plant goes as the 0.2 power. This indicates that extremely large size does not favour, and desalting plants will be found more feasible in modest sizes—100 to 500 mgd.

It is generally known that the nuclear desalination plant for fresh water production coupled with the manufacture of by-products, such as fertilizer and pure sodium chloride, results in much cheaper product costs equally with or less than market rates. Thus, especially, *a nuclear desalination plant in India not only fulfils its self-sufficiency in fertilizer production, but also eliminates or reduces greatly the foreign exchange.*

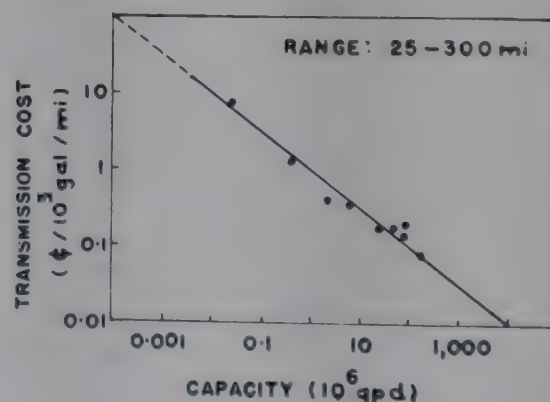


Fig. 8—Water Transportation.

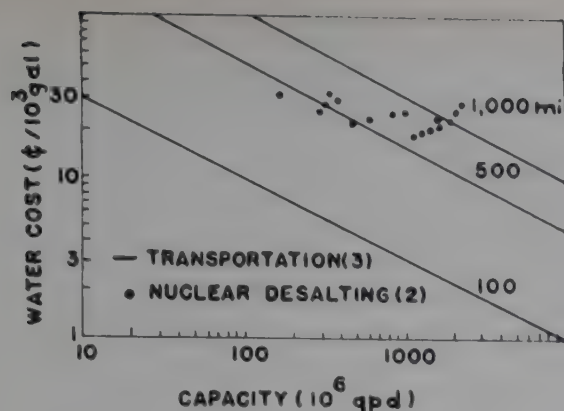


Fig. 9—Nuclear Desalting.

Proposal for a Nuclear Desalination Plant at Bombay

The chances and facilities for putting up a nuclear desalination plant in India are immense. Thorium, a nuclear fuel material is available in plenty on the coastal regions of Kerala. The field of nuclear technology is also fully developed, and the technical know-how could be contributed by our competent scientists. With such natural resources and technical know-how and with a view to meeting the immediate needs of fertilizer production, a nuclear plant for Bombay has been proposed below. The plant will be a dual-purpose one with provision of recovery of by-products like fertilizer and pure salt. Its detailed specifications and cost estimates have been based on the studies described earlier in this paper.

1. Required Plant Specifications:

Sea water input	= 150 mgd
Fresh water product	= 100 mgd

2. Design Details

Brine Concentration Factor	= 3.1
Salable power ¹³	= 750 Mw/day
Fertilizer production ¹⁶	= (Approx 40 tons/mgd sea water)
	= 6000 tons/day
	= 2.19×10^6 tons/annum
Pure Sodium chloride ²²	= (at 2% of sea water)
	= 3×10^6 tons/annum

3. Basis of Cost Estimate:

Capital Investment as given in Reference 12

3.1 Desalting Plant of 150 mgd capacity

Costs	= $\$94.2 \times 10^6$
In Rupee currency cost	= Rs. $7.5 \times 94.2 \times 10^6$

3.2 Power Plant As given in Reference 12

	= 185.50×10^6
Therefore	= Rs. $7.50 \times 185.50 \times 10^6$

3.3 Other Facilities as given in Reference 12

	= $\$ 38.50 \times 10^6$
Therefore	= Rs. $7.50 \times 38.50 \times 10^6$

3.4 Land Cost

Area requirement as given in Reference 11

1.37×10^6 sq. yards at the rate of Re. 0.75/sq. yard

3.5 Fertilizer Plant (all the items, a to d)

As given in Reference 16 and multiplied by a factor 10 from 15 to 150 mgd for direct proportion

- (a) Sulphuric acid $\$1.9 \times 10^6 \times 10$ (Rs. $7.50 \times 1.9 \times 10^6 \times 10$)
- (b) Phosphoric acid $\$1.9 \times 10^6 \times 10$ (Rs. $7.50 \times 1.9 \times 10^6 \times 10$)
- (c) Ammonia Stripping $\$2.6 \times 10^6 \times 10$ (Rs. $7.50 \times 2.6 \times 10^6 \times 10$)
- (d) Chemical treatment $\$4.2 \times 10^6 \times 10$ (Rs. $7.50 \times 4.2 \times 10^6 \times 10$)

3.6 In the absence of data, approximately done on 10% of the above total.

4 Annual Cost

4.1 Fixed charges on capital total investment

As given in Ref. (12) over a 30 year economic life

- (a) For non-depreciable capital (land) at the rate of 3.5% = Rs. (3.5%) (10,27,000)
- (b) For depreciable capital (349.9 crores) at the rate of 5.44% = Rs. (5.44%) (349.9)

4.2 O and M Power Plant as given in Ref. 12

$\$4.53 \times 10^6$ = Rs. $7.50 \times 4.53 \times 10^6$

4.3 O and M Desalting Plant as given in Ref. 12

$\$2.32 \times 10^6$ = Rs. $7.50 \times 2.32 \times 10^6$

4.4 Fuel Cost as given in Ref. 12

$\$21.59 \times 10^6$ (Rs. $7.50 \times 21.59 \times 10^6$)

4.5 Operation and Maintenance of Fertilizer Plant as given in Ref 16

$\$54.2$ /ton of fertilizer = Rs. $7.50 \times 54.2 \times 2.19 \times 10^6$

4.6 Manufacturing Sodium Chloride as given in Ref. (22)

DM 30/ton of NaCl (Rs. $1.87 \times 30 \times 3 \times 10^6$)

5 Income per Annum

- (1) Sale of power at the rate of Re. 0.15/kwh
- (2) Sale of fertilizer at the rate of Rs. 450/ton
- (3) Sale of pure NaCl as given in Ref. (22)
An average value of DM 70—DM 100, i.e. DM 85/ton
- (4) Sale of water to be adjusted
- (5) Nuclear fuel recovery buy back of plutonium as in Ref. 26 $\$8.00$ /g.

[Note:—(i) Multiplication factor 7.50 for the conversion of \$ currency; (ii) Multiplication factor 1.87 for the conversion of DM currency.]

6 Capital Investment

(1) Desalting Plant	Rs. 69,30,000
(2) Power Plant	Rs. 1,39,20,000
(3) Other facilities	Rs. 28,80,00,000
(4) Land Cost	Rs. 10,27,000
(5) Fertilizer Plant	
(a) Sulphuric acid plant	Rs. 14,25,00,000
(b) Phosphoric acid plant	Rs. 14,25,00,000
(c) Ammonia Stripping	Rs. 19,50,00,000
(d) Chemical Treatment	Rs. 31,50,00,000
Total	Rs. 3,16,90,27,000
(6) Recovery Plant for Pure Sodium Chloride (Say 10% of total)	Rs. 31,69,02,700
Total Investment Cost	Rs. 3,48,59,29,700
Or Say	Rs. 350 Crores

7 Annual Cost

(1) Fixed charges on Capital total investment	Rs. 19,00,36,000
(2) Operation & Maintenance on Power plant	Rs. 3,40,00,000
(3) Operation & Maintenance on desalting plant	Rs. 1,74,00,000
(4) Fuel Cost	Rs. 16,20,00,000
(5) Operation & Maintenance on Fertilizer Plant	Rs. 89,43,00,000
(6) Manufacturing Cost of Pure Sodium chloride	Rs. 16,83,00,000
Total Annual Cost	Rs. 1,46,60,36,000
Or Say	Rs. 146.60 Crores

8 Income per Annum

(1) Sale of Power (750 mw/day) at the rate of Re. 0.15/kwh	Rs. 17,10,937
(2) Sale of Fertilizer (2.19×10^6 tons/annum) at the rate of Rs. 450/ton	Rs. 99,00,00,000
(3) Sale of Sodium Chloride (3×10^6 tons/annum) at the rate of DM 85/ton	Rs. 47,68,50,000
(4) Sale of Water, 100 mgd	Not charged
(5) Nuclear Fuel buy back of plutonium at the rate of \$8.00/gram—Approx 1/3 of fuel cost (Item No. 4 in Annual Cost)	Rs. 5,00,00,000
Sale of Income per annum excluding	Rs. 1,51,85,60,937
Sale of water Say	Rs. 151.80 Crores

The cost estimate given above shows annual income at Rs. 151.80 crores without charging for water as against the annual expenditure of Rs. 146.60 crores with the capital outlay of Rs. 350 crores for a 150 mgd dual-purpose nuclear desalination plant. It is quite possible that the cost of power and other items can be reduced further by charging a marginal rate for water supply.

Nuclear power reactors are already in an advanced stage of development and certain types including light water, graphite and heavy water systems are available for industrial and commercial application on a competitive basis. These plants of established types can supply prime heat energy at a fuel cost of 10 to 15 cents per million Btus. But nuclear power costs are still dropping as a result of technical development and larger units. The application of breeder reactors and advanced converters, which will use thorium and heavy water reactors using organic substances or light water coolant, may still lower the costs to 5 cents per million Btus.

The total known 'monazite' resources of India exceed 5 million tons in which thorium is of the order of 5 lakhs tons as ThO_2 and 15,000 tons of uranium oxide (Indian monazite has a thorium content of 8 to 9 per cent, the highest in the world, and 1 per cent uranium. The reserves of thorium far exceed those of uranium). The flexibility characteristics of dual-purpose reactors should be investigated in detail. Also low temperature reactors may have useful application in the arid regions in the developing countries where *low power-to-water ratio* plants would be desirable.

One important item requiring investigations is reactor siting. Certain metropolitan areas situated close to the sea and having high electric power demand have begun to experience water shortage. The problem of air pollution resulting from use of fossil fuel would be solved by nuclear reactors, provided problems of safety are solved. To build dual-purpose plants far from city for supplying electrical power and water would entail a significant cost penalty for the transportation of water. It is necessary to develop proper design and engineering safeguards and review the siting criteria so that the dual-purpose nuclear stations may be built close to population centres without any hazard to the public.

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Notes & News

Catalyst for the Synthesis of Ammonia and its Production

The optimum performance from a NH_3 synthesis converter can be expected when the composition of the catalyst satisfies to the full the operating conditions—temperature, poison content of the gas, working pressure etc. The longevity of ammonia catalyst is also of utmost importance since replacing the catalyst always requires a shut down of the NH_3 -system lasting several weeks. Impurities in the feed gas are detrimental to catalyst activity. The types of NH_3 -catalyst more resistant to temperature and poisoning contain besides Al_2O_3 and K_2O , upto 3 per cent CaO and MgO , the high activity and therefore the more sensitive types, whether or not they contain other promoters beside Al_2O_3 and K_2O contain 1 to 1.5 per cent of CaO . More recently SiO_2 upto 1 per cent has been found of wider use. Thus a Bulgarian catalyst K-31 contains 3.9 per cent Al_2O_3 , 1.8 per cent K_2O , 2.3 per cent CaO , 0.4 per cent MgO and 0.8 per cent SiO_2 . Modern NH_3 synthesis units are designed to keep the synthesis converter temperatures below 500°C and CO content below 5 ppm. For catalysts operating under such conditions high contents of CaO and MgO are not useful. In addition to the concentration of promoter bivalent to trivalent iron has also an important bearing catalyst activity. Normally the iron oxide content ranges between 25 to 40 per cent.

Ammonia synthesis catalyst is made by melting different raw materials or by the recent method of sintering the well premixed components. In the melting technique natural or synthetic magnetite is the raw material; synthetic magnetite can be made by roasting pure iron in an oxygen current; the necessary flux (promoters) can be added to meet at this stage of the process. In most cases the synthetic magnetite obtained by melting is mixed thoroughly with promoters after cooling down, the mass then being melted down electrothermally. When natural magnetite is used it is mixed similarly with the promoters and then fused. In carrying out the melting

process care must be taken to ensure that the admixed promoters and magnetite form a homogeneous melt. The time taken for cooling the melt has a definite influence on the properties of the ammonia synthesis catalyst. Subsequently the cooled melt is reduced by crushing and screened to separate it into various size fractions. The grain sizes used with the NH_3 synthesis range between 4 mm to 24 mm.

Oxydic ammonia synthesis catalyst must be first converted into its active form by reduction. The catalyst produced by reduction is sensitive to poisons and to high operating temperatures. Since water is formed in the reduction the reduction must be carried out in such a way that only freely prepared high activity catalyst is in contact with water and then only for the shortest possible time. This is done by working with as high a space velocity as possible, taking care that the reduction temperatures are lower than the temperatures likely to prevail during synthesis. For safe control of the catalyst reduction, the water concentration in the gases leaving the converter should be kept as much as possible below the approximate upper permissible limit of 2 g./m³. The time necessary for the reduction can be shortened if a pre-reduced catalyst is used in the reaction zone first encountered by the gas.

A converter fed with pre-reduced catalyst can run into production immediately once the operating temperature has been reached whereas if an unreduced catalyst is used a reduction time of about 1 to 2 weeks will be needed.

The catalyst is removed by making its surface deactivated by treating with nitrogen to which an increasing amount of oxygen is added, otherwise the catalyst will heat up in contact with air.

[*Brit. Chem. Engng.*, 2 (11), 1967, 1743]

Compressor for Ammonia Synthesis

The development of steam-reforming processes, with natural gas or a relatively light oil (naphtha) as feedstock, eliminated the need for an oxygen plant and, with a

primary reformer requiring only steam needing only air, gives a synthesis gas at pressure 20-30 atm. At a synthetic loop pressure of 360 atm, the power required to compress the synthesis gas is only 60 per cent of that which would be needed to compress the same volume from atmospheric pressure; additional power is, of course, necessary to compress the air for the secondary reformer.

One of the first steps, though a relatively minor one, to effect some saving in the capital cost was the introduction of the multi-service (reciprocating) compressor in which all the services—air, synthesis gas refrigeration, recycle—were arranged on a single frame, thereby enabling savings to be made in the cost of buildings, foundations, electric motor, switch gear, etc. The total cost of the compressor section is, however, less than 10 per cent of the cost of the entire ammonia plant, so the economic effect of a multi-service is, in itself, quite small. It is now thought no longer essential to have spare equipment, particularly running machines. The view of the ammonia producers is generally that any plant—irrespective of its size—which uses reciprocating compressors must have at least two machines to ensure continuity of production.

Increasing the size of plant offers far greater potential for a reduction in capital cost than isolated technical developments. Doubling the size of a plant increases the cost by roughly 60 per cent. Compressor manufacturers were thus called on to develop design for machines considerably larger than those in use. In the U.K. preference had been for vertical compressors; in Europe and the USA for horizontal machines of the two crank tandem type. In the post-war years in the U.K. and Germany, compressors used for hydrogeneration of coal and oil could be switched to ammonia manufacture. In the USA the rapidly growing petrochemicals industry has led to the introduction of horizontal-opposed cylinder design of compressor, the advantages of which were quickly recognized, so much so that by mid-1950 the majority were able to offer compressors of this type for power upto 5000 hp.

But early in the present decade when the demand arose for compressors of significantly higher powers, manufacturers were generally unprepared. In the USA, it was met by retaining the single frame construction with appropriate modifications. Two compressors of this size, as multi-service machines, could cover an ammonia production of the order of 1500 t/d. In Europe, the compressor makers preferred to adopt H form in which the driving motor, is placed between two horizontal opposed machines, each of 5000-6000 hp. Its advantage was that it involved no extension of designs already known. Compressors of over 10,000 hp. are already available.

Experience in the petrochemical field had shown that purely rotating machines could be operated successfully for long periods "on line". The most important factor is the fact that petrochemical processes operate at a much lower pressure level and it was therefore possible to use centrifugal compressors. Various considerations led to the development of single stream ammonia plants, when the output is large enough to enable synthesis gas to be handled efficiently in a centrifugal compressor. At the same time the attainment of a high discharge pressure with the relatively light synthesis gas is facilitated by introducing the recycle gas at the inlet to the last stage. Subsequent developments have shown that provided the plant output is sufficiently large there is no inherent difficulty in achieving these pressures (300-350 atm.) in a centrifugal machine. Even designs for 450 atm. are available.

It is generally considered that for ammonia outputs below 550-600 t/d, a plant with 2 reciprocating compressors, though slightly more expensive in capital cost, compares favourably in total production cost with a single-stream centrifugal compressor, the difference in cost between the two types of plant increasing progressively as the output is reduced.

The only advantage which the reciprocating compressor can offer over its rival is flexibility.

[*Chem. and Proc. Engng.*, 49 (1968), 55]

Use of Liquid Sulphur Increases

Sulphur is fast becoming the element that is discussed along with nitrogen, phosphorus and potassium as being necessary for a complete fertilizer.

One example of increased use comes from the Western Ammonia Corporation in the

High Plains of Texas. It started incorporating ammonium thiosulphate in liquids on a trial basis in 1964. They produced 11-20-0-11S by mixing 11-37-0 and 12-0-0-26S. This grade accounted for less than 10 per cent of their liquid tonnage in that year.

By 1965, this grade accounted for almost one-third of their liquid sales. Slightly over 55 per cent of their liquid tonnage in 1966 went out as 11-20-0-11S. A slightly higher percentage has been used as 11-20-0-11S in 1967. Farmers liked the results from this NPS material and continued to use it in increasing quantities.

Research in Nebraska has shown the value of sulphur in liquid starter fertilizers. Including sulphur as ammonium thiosulphate in a liquid, 10-20-0 started produced an extra 20 bushels on an irrigated farm and an extra 10 bushels on a dryland plot. Following are the results: Sulphur sources for use in liquids are somewhat limited. The only clear liquid that is readily miscible in any proportion with neutral solutions is ammonium thiosulphate. It is readily miscible with nitrogen solutions as well as the NP and NPS clear liquids. Ammonium polysulphide is also a liquid sulphur source. It can be used for direct application but it is not miscible with the neutral solutions.

Ammonium thiosulphate has one unique characteristic from an agronomic standpoint, which possibly accounts for its good field performance. The thiosulphate ion will, upon application to the soil, form both sulphate and elemental sulphur in about equal proportion. The sulphate is readily available for plant use and will supply nutrient sulphur during the early part of the season. The elemental portion is in a very finely divided colloidal state and consequently is readily oxidized to sulphate during the growing season. This "reserve" provides nutrient sulphur during the middle and late part of the growing season. Thus, the plant has a ready supply of sulphate-sulphur throughout the season.

Crop response to thiosulphate occasionally appears to be better than responses to other forms of sulphur. It has been suggested that thiosulphate influences soil pH and thereby increases phosphorus, iron, zinc, manganese availability in alkaline, calcareous soils. Results of field trials have indicated that a combination of phosphorus and sulphur is often needed to get response to either nutrient in highly calcareous soils. Because of rapid plant response to thiosulphate, the

possibility arises that there is a direct uptake of the thiosulphate ion.

[*The World of NPKS*, No. 18, December 1967, 21.]

Modified Ammonia Process From C.F. Braun and Co.

A new process introduced by C.F. Braun and Co. for ammonia manufacture is reported to be in successful operation. In this process excess of air in addition to that required for the 3:1 ratio of hydrogen to nitrogen in ammonia synthesis, is added to the secondary reformer in the synthesis gas section of the plant. This permits greater independence of operation between the synthesis gas section and the ammonia synthesis section. The excess air i.e. nitrogen is removed from the gas stream by a cryogenic purifier just prior to the gases going to ammonia synthesis; this purifier also removes contaminants from the unreacted gas that is recycled from the ammonia-production reactors.

Also of direct value at the primary reformer is the system for feeding the excess air to the secondary reformer. The air compressor feeding the secondary reformer is driven by a gas turbine that operates at high efficiency by taking more air than necessary into its own combustion chamber; this pre-heated air from the combustion chamber is discharged as combustion air for the primary reforming furnace.

The amount of excess air fed into the secondary reformer reduces the reaction burden in the primary reforming furnace. The purified gas leaving the unit and passing to ammonia synthesis will be in vapour-liquid equilibrium with the impurities condensed out at the operating temperature and pressure. The low temperatures involved 285°F suggest that materials of construction have to be carefully considered.

In the process flowsheet, natural gas feed goes to the primary reformer conventionally. This reformer operates at about 1,350°F and 430 lb/in², and leaves some 20 per cent of the methane unconverted (8-9 per cent in usual ammonia practice). This methane is then reacted in the secondary reformer, in a partial-oxidation type reaction, at about 1,650°F under such conditions that the synthesis-gas purification has a hydrogen-nitrogen ratio of around 2:1.

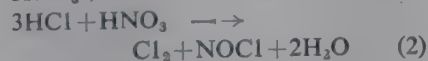
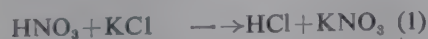
Carbon monoxide and steam are converted to hydrogen and carbon dioxide in

conventional shift reactors; carbon dioxide is removed in usual-type scrubbers; residual traces of carbon monoxide are converted to methane in a conventional methanator; the synthesis gas is then dried and fed to the cryogenic purifier, where the excess nitrogen plus 99 per cent of the remaining methane are removed. Hence the gas for ammonia synthesis is purer than the usual feed.

[*Nitrogen*, No. 50, (1967), 41]

Potassium Nitrate Manufacture

Preparation of potassium nitrate by the reaction of potassium chloride with nitric acid has not so far been used on a large scale because of side reactions that occur and produce chlorine and nitrosyl chloride.



Kuhlmann has recently been granted a patent (B.P. 1,077,073) for the manufacture of potassium nitrate using the overall effects of reaction (1) without suffering the drawbacks of equation (2). In addition, ternary fertilizers can be produced, by combination of potassium chloride, phosphoric and nitric acid and ammonia.

The process initially involves the heating of potassium chloride and phosphoric acid to produce monopotassium phosphate and hydrogen chloride to obtain the maximum amount of mono-potassium phosphate. 50 to 100 per cent by-weight in excess of the stoichiometric amount of phosphoric acid is used and the ideal temperature for the reaction is about 200-400°C, although an upper limit of 700°C is quoted. Agitation is provided with the dual purpose of mixing the reactants and also assisting with the evolution of the hydrogen chloride. Air can be bubbled through the reaction mixture to remove hydrogen chloride or alternatively, the reaction can be carried out at a slightly reduced pressure.



A slight excess of aqueous nitric acid is now added and potassium nitrate is formed. It is sometimes necessary to add a small amount of water to bring the concentration of orthophosphoric down to 75-85 per cent by weight.



The potassium nitrate is crystallized out by cooling the solution down to room

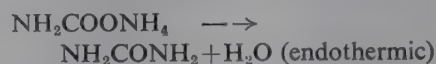
temperature, or better still 0°C, when a better crystallization yield is obtained. The potassium nitrate crystals are separated from the mother liquor by either filtering or centrifuging or alternatively, a ternary fertilizer can be manufactured. In this case, an aqueous slurry containing potassium nitrate, phosphoric and nitric acid is neutralized with ammonia to produce a fertilizer of approximately 19-19-19 composition. The ammoniation is carried out in a rotating tube until a powder or granules of pH 6.7-6.9 are obtained, the heat developed by the neutralization contributing to the drying of the product.

The phosphoric and nitric acid containing mother liquor can be recycled, or alternatively may be used for the manufacture of other fertilizers by reaction with phosphate rock.

[*Phosphorus & Potassium*, No. 32, (1967) p., 47]

Stamicarbon's Process for Making Urea

Stamicarbon N.V. of The Netherlands has developed a new stripping process for making urea with lower investment and operating costs as well as fewer maintenance problems. The chemical reactions involved in the method remain unchanged:



But the difference lies in the way the company removes unwanted carbamate from the reactor effluent.

In the stripping process, unreacted carbamate and excess ammonia present in the effluent stream are removed by stripping with carbon dioxide. Energy is thus conserved because the stripped gas stream, at a relatively high temperature, is used to raise low-pressure steam through the concentration of its ammonia, carbon dioxide and water vapor. Moderate temperature is maintained to reduce severe corrosion problems.

One interesting feature of the Stamicarbon method is that the reactor, the stripper and the condenser operate at the same pressure (1,910 psi.). This means that the stripping process must use a lower NH_3/CO_2 ratio (2.0) than normal (4.0). As a consequence, it obtains less CO_2 conversion per pass in the reactor.

Stamicarbon points out that this apparent disadvantage is offset by two important gains. By using a 2.0 ratio, the conden-

ser operates under optimum conditions, and, by working at basically the same pressure in the reactor, stripper and condenser, the plant operates by gravity flow without the need for compressors or pumps to circulate potentially corrosive streams.

In the Langelshheim plant of W. Germany which is following this method for manufacturing urea, ammonia and carbon dioxide are not mixed directly in the reactor. Instead, carbon dioxide is first routed through the stripper, where it removes part of the excess ammonia and carbamate. After passing through the high pressure condenser, the CO_2 enters the reactor along with condensed, recycling carbamate.

The reactor is a hollow, stainless steel-lined vessel provided with an overflow pipe for taking off the product mixture. Stainless steel is also the material of choice for other high-pressure equipment (stripper, condenser). The material is protected against the corrosive action of the reaction components by Stamicarbon's patented technique of injecting a controlled amount of oxygen along with the carbon dioxide feed.

Products from the reactor pass to the stripper, a shell-and-tube heat exchanger provided with a good gas-liquid distribution system. The stripper receives CO_2 at its lower end, and is heated by steam at 300 psig. From its top, a gas stream containing most of the unconverted carbamate (as CO_2 and NH_3) and the excess ammonia is recycled via the high-pressure condenser to the reactor.

In the condenser, the unconverted gases serve to turn boiler-feed water into low-pressure steam. This steam is reused in several evaporators throughout the plant.

From the bottom of the stripper, a urea solution containing residual carbamate and ammonia passes through an expansion valve and enters a low-pressure rectifier. From here, it passes through a heater and then through a separator. A flash tank follows, wherein the temperature of the urea solution is reduced by means of lowering the pressure. The urea is sent to an intermediate storage vessel, where it is kept in the form of a 75 per cent solution at moderate temperatures.

Concentration Step: From hereon the process follows the traditional method. The dilute urea solution can be concentrated in two evaporation stages to approximately 99.8 per cent before prilling; the prills have a biuret content of about 0.7 per cent.

They must not be exposed to exhausts from petrol and diesel engines, or to heat

The consumption figures of Stamicarbon method are as follows:

Carbon dioxide	1,660 lb.
Ammonia	1,254 lb.
Steam (350 psig.)	2,200 lb.
Steam (45 psig.)	330 lb.
Cooling water (77°F.)	14,528 gal.

[*Chemical Engng*, 75 (2), 1968, 132]

Manufacture of Hydroxylamine by Catalytic Reduction of Nitric Oxide

Catalytic production of hydroxylamine from nitric oxide upto the plant scale size is now possible by a process recently developed by Badische Anilin and Soda Fabrie AG., Ludwigshafen/Rhein. High percentage nitric oxide required for the process may be obtained either from nitric acid when reacted with sulphur or from ammonia. In the process of producing nitric oxide from ammonia a mixture of ammonia, steam and oxygen enters a reactor where ammonia is oxidized over platinum rhodium catalysts. The reaction heat is recovered in the waste heat boiler. The produced gas mixture consisting of nitric oxide, steam, excess oxygen and some nitrogen dioxide is mixed with hydrogen. In another reactor the oxygen is catalytically reduced to water and the nitrogen dioxide to nitric oxide. The steam is condensed in a condenser. The residual nitric oxide is again mixed with hydrogen and catalytically reduced to hydroxyl ammonium sulphate in a third reactor which is filled with a suspension of platinum-Catalyst in dilute sulphuric acid. The produced hydroxyl ammonium sulphate solution is taken out of the system through a filter. The offgas goes to a flare.

The reaction rate is increased by increasing pressure and a temp. above 40°C is maintained. The rate of reaction decreases with initial acid concentration, increasing salt of the liquid medium, and at a constant SO_4 -concentration.

The hydrogenation of nitric oxide may be controlled so as to favour either hydroxylamine or ammonia formation, as (a) increasing pressure favours hydroxylamine formation; (b) elevated temperature favo-

urs ammonia formation. (c) contrary to expectation, an increase in the molar ratio of $\text{H}_2:\text{NO}$ favours hydroxylamine formation rather than ammonia formation; (d) an increase in the initial acid concentration favours ammonia formation; (e) at a constant SO_4 -content, ammonia formation is favoured by decreasing H^+ ion concentration; and (f) reaction control via the catalyst is of special interest. As it is not desired to discuss the influence of catalyst geometry, e.g. specific surface area, or methods of manufacture, only the possibility of partial poisoning is mentioned here.

The new BASF hydroxylamine process has the following advantages: The hydroxylamine solution obtained has higher purity and a higher concentration. The process can be operated so that no nitric acid is formed as by-product. Less ammonium sulphate is obtained in processing the solution and the ammonium sulphate is pure white and free from impurities. The oxime is of excellent quality. The overall yield of hydroxylamine, based on ammonia, is greater than 85 per cent.

Reaction of hydroxylamine or its salts with cyclohexanone gives cyclohexanone, an intermediate in caprolactum manufacture. With a production of one million tonnes of caprolactum per year as estimated for 1970 using the conventional variants of the Rasching process some 47 million tonnes of ammonium sulphate would be obtained per year as byproduct. With the BASF process the amount would be approximately 2.6 million tonnes, including approximately 2 million tonnes obtained in the Blackmann rearrangement of cyclohexanone oxime. Another advantage is that with the higher temperature level, the heat generated in the hydroxylamine reaction can be removed with ordinary cooling water.

[*Nitrogen*, No. 50, Nov/Dec. (1967), p. 27]

Nitrophosphate Fertilizer

A Norwegian firm is setting up a modern 1,500/day nitrophosphate plant based on Odda process incorporating several major improvements—controlled crystallization of calcium nitrate, step by step neutralisation of the mother liquor and a new prilling process developed by Norsk Hydro of Norway—to obtain a wide range of fertilizers. Water solubility of the P_2O_5

contained in the fertilizer by this process will be increased to about 85 per cent by removing as much unwanted calcium nitrate as possible.

In this process phosphate rock is reacted with nitric acid, forming phosphoric acid and calcium nitrate. The latter compound is crystallized, and later converted to ammonium nitrate and calcium carbonate by being reacted with ammonia and carbon dioxide, or it may simply be concentrated and prilled to a nitrate of lime fertilizer containing 15.5 per cent nitrogen.

Meanwhile, the mother liquor that remains after calcium nitrate crystallization is neutralized with ammonia and converted into NP liquor. The latter is stripped of its water content in an evaporator, mixed with a potassium salt, and then prilled, cooled, screened, and mixed with a coating agent. More than 95 per cent by weight of the resulting prills measure between 1 and 4 mm. dia.

The equipment used for the acidulation of the phosphate rock is a simple stainless-steel vessel provided with an agitator. If a low-grade phosphate is employed, a sand trap is placed after the vessel to remove undissolved matter such as sand.

The crystallization and removal of the calcium nitrate tetrahydrate is basically a batch process involving a number of crystallizers operated in cycles, giving an over-all effect of continuous operation.

The crystals obtained are of uniform size, thus forming an open filter-cake. The mother liquor, which contains fine undissolved impurities, is filtered on a continuous rotating filter provided with a stainless steel cloth that has openings of about 5 mm. This filter is a special design of Norsk Hydro; it is a compact, high-capacity unit that operates under a moderate vacuum. After filtration, the crystal cake is washed with nitric acid, and then with a small amount of water.

The final crystallization temperature determines the degree of calcium nitrate removal, and also the water solubility of the phosphate in the final product. Since recent demand has been for higher water-solubility, Norsk Hydro crystallizes at around 23°F. This involves removing about 1.4 million cal./ton of phosphorus, which adds to the refrigeration cost.

Neutralization is carried out by raising pH of the solution in three steps to about

liquor, and the resulting slurry is prilled. The prilling tower, of special design, is made of concrete. From 1,500 to 2,000ton/day can be prilled in a single tower 120 ft. high and 60 ft. dia.

The hot concentrated liquor is sprayed as fine droplets and cooled with air to about 176°F. The prills are further cooled to 122°F. and coated before going to storage. In addition to yielding high capacity in one train, prilling creates low recycle (usually less than 5 per cent of the product), and eliminates subsequent drying. It also is said to offer better control of product composition than does conventional granulation.

[Chem. Engng., Oct. 23, (1967), p. 134]

Pop-Up Fertilizers with Phosphorus may Create Zinc Deficiency in Corn

Recent investigations have shown that the use of phosphorus fertilizers tends to depress the zinc content of corn, lowering yields and delaying maturing of the corn plants. The lack of balance between phosphorus and zinc is generally associated with soils that are medium to low in available zinc. A high level of available potassium tends to offset somewhat the unfavourable effects of phosphorus on zinc

in the growth of corn.

It has been found that the combined application of phosphorus and zinc sulphate in starter fertilizer has generally produced higher yields of corn than the application of these nutrients alone. As a general rule one can apply annually 1 lb. of zinc (approx. 3 lbs. of zinc sulphate) for 10 lbs. of P_2O_5 in the fertilizer for fields considered to have phosphorus-induced zinc deficiency. In alkaline soils (pH above 7) zinc becomes fixed as hydroxides, carboates and phosphates. Soil management procedures can be followed to keep much of the zinc in an available form where zinc fixation is a problem annual application of zinc sulphate are generally necessary.

After application of zinc sulphate to the soil, zinc tends to remain where it is placed. This is especially true of soils of alkaline reaction. To be effective, the zinc must be placed either below the seed or at the same level as the seed. Starter fertilizers containing zinc sulphate and phosphorus are effective if applied in a band at or slightly below the seed level at planting time or broadcast and plowed under the surface zinc sulphate should always be applied with a nitrogen source, since nitrogen enhances the uptake of zinc by corn plants.

Storage of Fertilizers in The Farm

General Recommendations: All fertilisers must be properly stored, so that they will keep their spreading properties even after long storage. The demand for concentrated fertilisers in advanced farming makes it necessary to be aware of some main rules for handling and storage.

Since most fertilisers tend to absorb moisture from the air, they must be stored in dry places or otherwise protected against damp. Storage buildings must have watertight roofs come into direct contact with the fertilisers should, if necessary, be made water-proof with protective coatings or plastic sheets.

Sacks containing fertilisers must be carefully stacked. The stacks must be stable and secure against collapse. Damaged sacks should be repaired or the contents transferred immediately to undamaged clean sacks of similar type. Bulk fertilizers should be covered with tarpaulins or plastic sheets (seek suppliers' advice). Open fertilisers must not be accessible to animals.

If bagged fertilisers are stored in the open, they must be protected against rain and direct sunlight by covering, for instance, with plastic sheets. The storage area should be smooth and self-draining.

In the storage of those fertilizers which contain ammonium nitrate, special care should be taken. If these fertilisers are heated by external heat or fire they may decompose with evolution of yellowish-brown, poisonous fumes. With some compound fertilisers, this decomposition, once started, can slowly spread throughout the whole mass of the fertiliser. This decomposition can be fought only with water.

Properly stored, the fertilisers represent no hazard. To avoid decomposition the following recommendations should, however, be observed.

Special Recommendations: Before the fertilisers are put into store, especially in bulk form, the storage space must be clean. Oil, sawdust, grain refuse, straw or other combustible materials and acids must be kept away from the fertilizers. Smoking and the use of open fire in the store must be forbidden.

Fertilizers must not be heated. They must not be left in contact with heating equipment, steam pipes (even when insulated), electric lamps, motors or cables.

Recommended Rates of Application	Rate of Appln./Acre*	
	Calculated as Zn	Calculated as Zn sulphate
Mild zinc deficiency. These may be soils medium to high in phosphorus: Little or no top soil removed. Plants showing little or no zinc deficiency symptoms but responding in growth, maturity and yield to zinc applications, particularly where starter fertilizer is used.	2-5 lbs.	5.5-13.7 lbs.
Slight to moderate zinc deficiency. Acid, neutral and alkaline soils. No free lime, low organic matter content.	5-10 lbs.	13.7-27.4 lbs.
Moderate to severe zinc deficiency. Alkaline soils with free lime (calcareous). Low organic matter content.	10-20 lbs.	27.4-54.8 lbs.

*The higher rate of zinc application should be applied to alkaline soils (pH above 7.0) with free lime (calcareous). it may be necessary to increase these rates for complete correction of zinc deficiency in growing seasons following prolonged cold spells in spring or early summer. Generally zinc should always be used on land levelled for irrigation or graded for terraces, or following a crop of sugar beets. It should always be applied with a nitrogen source (either with a straight material or together with phosphorus or phosphorus plus potassium).

[Farm Chemicals, 130 (12) (1967) 46]

six in order to control viscosity and the precipitation of residual calcium.

The heat of neutralization, 1,250 cal./ton of ammonia evaporators some water from the liquor. The latter retains 15 per cent water, and exists at a temperature of 266°F.; but further evaporation reduces the final water content to about 0.5 per cent.

Both potassium chloride and potassium sulphate, in addition to micronutrients, can be mixed with the concentrated NP-generated by portable heaters or lamps or by welding and cutting operations. Caked fertilizers should be broken up by mechanical means only. The use of explosives must be forbidden.

In the event of a fire breaking out near the fertilizers, it must be extinguished by the most effective means available. Adjacent fertilizers must be protected from heating by spraying it with water.

If decomposition of the fertilizer is started, it will be recognized by the appearance of white or brown fumes, which must not be inhaled as they may be poisonous (nitrogen oxides). However, if the affected part is still small and accessible, an attempt may be made to get it away from the remainder and to cool it with water or by spreading it in the open air. Other means (carbon dioxide, foam, covering with sand or with fertilizer) are ineffective.

Greater areas of decomposition can be fought only with large quantities of water. The local fire brigade should, therefore, be called. The fumes should not be entered without independent breathing apparatus.

[FAI Information Serv., 9 (8) (1968), April 16]

An Integrated Coal-Fertilizer Complex in Assam*

Reserves of Assam coal are estimated at 3,800 million tons. This coal is very low in ash and is relatively high in hydrogen and sulphur contents. On carbonization per ton of it yields 40 to 50 gallons of tar which could be hydro-refined to get middle distillates. The recovery of sulphur could also be an added advantage. Thus, pro-

perties of the Assam coal are suitable for processing into chemicals and fertilizers. Regional Research Laboratory, Jorhat (Assam) proposes a scheme* with an investment of Rs. 67 crores and the end-products contemplated in the scheme are ammonia, phenol, diesel oil, petrol, pitch, ammonium sulphate worth Rs. 44 crores per year. The recurring expenses estimated are Rs. 17.67 crores. Thus the scheme leaves a bare margin of Rs. 26.48 crores per annum.

There is no other factory producing fertilizers in Assam except at Namrup run by the Fertilizer Corporation of India Ltd. The present capacity of the plant is 55,000 tons of urea and 1,00,000 tons of ammonium sulphate. The total dosage of nitrogen recommended for Assam soil is 86,500 tonnes per year and therefore, present Namrup production leaves a deficit of about 50,000 tons of nitrogen. The Namrup plant uses natural gas as feedstock. The report says that the duration of the availability of gas is also short i.e. about 10 years or less. Considering the future demand for this raw material, RRL proposal maintains that total availability of gas will not keep pace with the future consumption. Therefore, it is imperative, says the report, to switch on to an alternative source like coal.

The scheme further puts up a proposal for setting up an additional capacity of 22,000 tons of nitrogen per year with capital investment to the tune of Rs. 13 crores. The annual recurring expenditure envisaged is Rs. 3 crores and end-products worth Rs. 4.6 crores will be obtained thus giving a profit of Rs. 1.6 crores per year.

The technical details and financial outlay for the scheme are as follows: The scheme consists of two steps i.e. devolatilization of 2,000 tons of Assam coal in a fluidized bed and processing of by-products to middle distillates and gasification of the fluidized char for ammonia synthesis for the production of ammonia, ammonium sulphate and urea.

(1) *Devolatilization*: The 6 x 0 coal received at the plant is crushed to $\frac{1}{4}$ " size in a hammer mill and to -36 mesh in a roller crusher and placed in temporary storage in concrete silos. From the silos, the material is pneumatically conveyed to an alloy steel reactor, 6 ft dia. and 35 ft. in height mounted in a special furnace which is equipped with equilibrators for efficient operation and pre-heating of process and combustion

air. The process air is compressed to about 8 psi and passes through a recuperator, where it is preheated to about 700°F. The mixture of air and coal enters the base of the reactor and the fine coal is moved up through the reactor entrained in the products of reaction in a turbulent condition. The temperature of the product leaving the reactor at the top is controlled automatically by regulating combustion around the reactor or by regulating the air-coal ratio. The char is separated through a series of cyclones and conveyed pneumatically to a char silo. The tar-laden gases pass through a series of condensers and electrostatic precipitators for recovery of the tar and other by-products.

(2) *Gasifier*: The char obtained from the devolatilization plant is partly blended with calcined dolomite and conveyed by high pressure superheated steel to the gasifiers where 60 per cent of the carbon in the char is gasified at 1600°F for the reaction $C + H_2O \rightleftharpoons CO + H_2$. The remaining char and the dolomite streams together are withdrawn from the gasifier bed and conveyed with compressed air to regenerators where most of the carbon is burnt out to supply heat for the calcination of the dolomite. The residual char and particle ash are removed overhead by means of cyclones. The calcined dolomite is recycled to the gasifiers.

The regenerator off-gases contain sufficient sensible heat to generate all the superheat steam required by the gasifier. It can be further utilized for generation of the necessary power. The resultant gas is then freed of sulphur by passing through a bed of limestone. The sulphur-free gas is then divided into two parts: (i) is mixed with the reformed gasification gas and is then processed for the removal of carbon dioxide and carbon monoxide and (ii) the purified gas ($N_2/H_2:1/3$) is then synthesized to ammonia in a converter. The rest of the gas is vented out. The manufactured ammonia is mostly used for the production of ammonium sulphate and urea. The ammonium sulphate manufactured only corresponds to the sulphur recovered from the complex as calcium sulphate. The carbon dioxide needed for the urea is obtained both from the gasifier gas and from the regenerator gas.

The tar obtained from the fluidized carbonization is fractionated in a column and then after removal of the tar acids hydro-refined to give the middle distillates.

*Outline of a Proposal for Setting up an Integrated Coal-Fertilizer Complex in Assam Valley (Regional Research Laboratory, Jorhat, Assam), November 26, 1967.

Estimated Investment Cost of the Project

Combined Complex Cost

(Rs. in crores)

1. A. Fluidised Low Temperature Carbonization including distillation and hydro-refining	14.785
B. Gasification	8.100
C. Gas Reforming	7.000
D. Ammonium Sulphate Production Unit	11.800
E. Urea	7.670
F. Cost of dolomite	0.072
	<hr/>
	49.427
	<hr/>
2. Civil construction for all plants including factory and non-factory area @ 3% of the plants cost	16.600
3. Working capital (3 months)	0.800
	<hr/>
Grand Total	66.827
	<hr/>

Annual Recurring Expenditure (Combined Plant)

1. Raw Materials	1.9094
2. Utilities	0.8880
3. Staff	0.0800
4. Maintenance and Total depreciation	8.1370
5. Return on Capital Investment @ 10% on Rs. 66.827 crores	6.6827
	<hr/>
Grand Total	17.6971
	<hr/>

[Note: The generated steam can be utilized for gasification and drying purposes provided a separate thermal power plant of 50 MW capacity be set up near the complex. In that case an additional investment of Rs. 5 crores shall have to be added to the capital cost.]

Income

Product	Total Production (Tons)	Rate (Rs./Ton)	Income in Rs. crores
1. Ammonia	44,700	800	3.5800
2. Phenol	15,300	525	0.8032
3. Diesel Oil	48,840	640	3.1260
4. Petrol	1,800	750	0.0135
5. Pitch	30,000	250	0.7500
6. Ammonium Sulphate	43,800	400†	1.7520
7. Urea	683,100	500††	34.1550
			<hr/>
	Total Output/Year		44.1797
			<hr/>

†The import price per ton of ammonium sulphate =Rs. 474.23

††The import price per ton of urea =Rs. 825.57

Profit

Income	Rs. in crores
Expenditure	44.1797
	17.6971
Profit	26.4826

Investment Needed for the Manufacture of 22,000 Tons of Nitrogen Per Year Based on Assam Coal

	Rs. in crores
1. Capital Investment for Plant and Machineries	9.638
2. Civil Construction	3.213
3. Working Capital (3 months)	0.052
Grand Total	12.903

Annual Recurring Expenditure

1. Raw Materials	0.1000
2. Utilities (power, water, etc)	0.0500
3. (i) Maintenance & depreciation on plants and machinery (ii) Interest on working capital on 0.052 crores	1.3030
4. Depreciation on Civil Construction	0.2740
5. Return on Capital Investment	1.2960
Total	3.0230

Products/Year

			Rs. in crores
1. Phenol	990 Tons	@ Rs. 525/ton	0.0519
2. Diesel Oil	31700	„ @ Rs. 640/ton	2.0300
3. Petrol	117	„ @ Rs. 750/ton	0.0088
4. Pitch	1950	„ @ Rs. 250/ton	0.0500
5. A/Sulphate	2847	„ @ Rs. 400/ton	0.1140
6. Urea	46880	„ @ Rs. 500/ton	2.3440
Total Recovery			4.5987

Profit: Rs. 4.5987—Rs. 3.0230=Rs. 1.5757 crores

Editor's Comments

The statement regarding the availability of natural gas for a period of ten years or less requires further critical study and examination. The proposed expansion of the Namrup fertilizer plant based on natural gas and extensive investigations of ONGC should allay any undue apprehension. Further, it appears that the report has not taken into consideration the 330,000 tonnes/year of urea expansion of Namrup fertilizer plant which has already been approved: its implementation has been taken up and this additional capacity is expected to go into production by the end of Fourth Plan. This further

expansion of urea will meet the entire nitrogenous requirement of Assam. We, therefore, feel that any further additional fertilizer production in Assam, would have to be considered only from the point of possible movement into other parts of India for consumption.

India has large coal deposits in different parts of the country including Assam. There is every possibility that the coal-based fertilizer production could be more advantageously resorted to in other parts of India than Assam since such locations would be favourable for economic product distributions. The only factor which appears in favour of location in Assam is

the availability of sulphur in Assam coals. According to the RRL proposal, the sulphur available in the coal expected to be consumed in the complex would enable production of 43,800 tonnes of ammonium sulphate. This would correspond to about 10,000 tonnes of sulphur annually. On this assumption the distribution of the product manufactured in Assam in other parts of India would involve additional freight of about Rs. 50 per tonne. Therefore, location in Assam would involve distribution expenses of about Rs. 4.3 crores more than in case the complex is located in other parts of India like Madhya Pradesh or Andhra Pradesh. Will this additional incidence of freight or distribution justify the location of the complex in Assam merely to enable the availability of 10,000 tonnes of sulphur in the form of gypsum for conversion of ammonium sulphate? In this connection it may also be noted that a proposal for a large nitrogenous fertilizer product based on coal to be located in Madhya Pradesh is already with the Government of India for consideration. Another proposal for a similar plant in Andhra Pradesh is also under preparation.

Further, from a preliminary analysis, it appears that the investment requirement of the project is likely to be substantially higher than has been estimated in the proposal. The investment requirements including civil construction indicated for the gas reforming and the urea plant are much lower than the normal levels of costs. There is no provision in the estimate for facilities other than the main plant, as for example, the steam generation plant, railway facilities, water supply and treatment facilities, etc. The investment figures do not include financing charges, expenses during construction etc.

There is no provision towards cost of steam necessary for the ammonium sulphate and the urea plants. It is expected that the urea plant alone would require steam to the extent of 150 tonnes per hour. The allocation of Rs. 8 lakhs per year towards wages and salaries is indeed small, specially considering that the facilities would be based on the use of solid fuel as the feedstock. There is no consideration for annual recurring expenses towards the cost of catalyst and chemicals. The estimates also do not include the cost of bagging the products. Moreover, the plant capacities envisaged the coal requirement of 6 lakhs tonnes per year seems to be substantially lower than what may be necessary even for straight gasification.

Reply to the Editor's comment by Dr. M. S. Iyengar, Director, Regional Research Laboratory, Jorhat (Assam)

We agree that a critical assessment of the availability of the gas should be undertaken but regret to find that a decision has already been taken to expand the fertilizer capacity based on gas without fully going into the availability aspect. The amount of gas available is low and the period for which it is likely to be available is also low. Because of this, The Fertilizer Corporation of India has amortized the gas-based fertilizer plant at Namrup for 10 years which would necessarily give only high cost fertilizers.

The availability of the limited amount of gas can be extended for a longer period by re-compressing and censoring the gas but such measures are likely to increase the cost of gas to the consumer. For example, it is understood that the price of the gas to fertilizer has been fixed currently at Rs. 1.50 per thousand cu. ft. This may go up upto Rs. 6 per thousand cu. ft. If the gas is to be conserved by recompression, whatever advantage can be obtained by amortization charges be compensated by the increase in raw material cost. Also such a price would be well above the general level of the gas prices prevalent in most of the other countries in the world. If further quantity of gas is to be made available from Rudrasagar and Sibsagar area, gas has to be conveyed for a distance of about 100 miles which would entail installation of pipeline and pumping facilities at extra installation costs. Further, in view of large quantities of fertilizers required elsewhere in the country and the Government thinking of importing it in substantial quantities, there should not be any difficulty in considering movement of fertilizer either in the form of ammonia or urea from Assam to other parts of the country.

It is true that India has large coal deposits in different parts but, the coals found in Assam are unique, the like of which are not found in the rest of the country.

The following are the advantages in locating the coal-fertilizer complex in Assam in preference to M. P. or Andhra Pradesh: (i) The coal has a very low percentage of ash (4%) and even this ash is very rich in germanium. (ii) The carbonization properties of Assam coal are compared in the following table with those of M. P. and Singareni coals.

COMPARISON OF CARBONIZATION
PROPERTIES OF ASSAM COAL

Coals	Coke	Tar
M.P. (Bisrampur)	73.7	8.0
Raniganj Coalfield (Kajora seam)	66.9	16.8
Singareni (A.P.)	67.5	8.5
Assam Coal (Baragolai Coalfields)	57.3	19.2
Jharia Coal (Bararee XIV seam)	77.2	12.1

It would be seen that Assam coal produces total 3 times as much tar as the other coals from which substantial quantities of middle distillates and tar acids could be obtained. In addition, Assam coal contains sulphur which is not the case with other coals. If the by-products listed in the project are taken into consideration, their yield is higher and better than those obtained from other coals which could make a significant effect to the project.

The proposed complex would utilize, as stated in our project report, 6.0 lakh tonnes of Assam coal and will involve not only simple gasification but also devolatilization and recovery of valuable by-products followed by subsequent gasification of the char. The low ash content of these coals gives an additional advantage. In fact, though the anticipated requirement of 6.0 lakh tonnes of coal/year, apparently appears to be low for such a big complex as mentioned by you, the ash percentage

will clearly point out that it is equivalent to approximately 7.2 lakh tonnes of M.P. and A.P. coals.

It may be necessary to market the chemical and the fertilizer in other parts of the country and will certainly involve an additional increase of Rs. 50-60/tonne in freight, but, as the complex will yield a good number of valuable by-products like sulphur, middle distillates, tar acids, pitch etc., these will contribute to the improved economy of the project and compensate for the cost involved in transportation.

As regards your comments on the requirement of steam, we may refer to our proposed process as given in the flowsheet diagram.* The process includes the generation of steam required for the whole complex and as such no separate steam generation unit is included.

We fully agree with you that we have not included the recurring expenses towards catalyst, its losses during the process and packaging the final products. This will at the most involve an additional amount of Rs. 15/- per tonne on the finished product.

We have taken the life of the plant, as usual, for ten years and the depreciation has been calculated accordingly.

The coal reserves in this region are of the order of 3,800 million tons. Their exploitation for fertilizer production needs all the necessary encouragement as in addition to providing the synthesis gas they also provide sulphur and a host of other products. Comparative cost of production of one ton of ammonia based on different coals and natural gas is given on the next page.

*Flowsheet diagram. appearing in the original report is not included in our summary

—Editor

COMPARATIVE COST OF PRODUCTION OF ONE TON OF AMMONIA BASED ON COALS FROM ASSAM* (A), SINGARENI (B) (A.P.) AND BISRAPUR (C)† (M.P.) AND NATURAL GAS‡ (D)

	(A) in Rs	(B) in Rs	(C) in Rs	†(D) in Rs
1. Cost of raw material	49.00 (1.4 tons @ Rs 35/- ton)	66.50 (1.9 tons @ Rs 35/- ton)	61.25 (1.75 tons @ Rs 35/- ton)	26.00 (17,500 cu.ft. @ Rs 1.5/ 1000 cu. ft)
2. Power and steam	53.00 (@ 0.06/ kWh)	53.00 (@ 0.06/ kWh)	53.00 (@ 0.06/ kWh)	60.00 (@ 0.06/ kWh)
3. Salary and wages	115.00	115.00	115.00	38.00
4. Fixed charges on capital 20%	175.00	175.00	175.00	140.00
Total	392.00	409.50	404.25	264.00

RECOVERY OF BY-PRODUCTS PER TON OF AMMONIA PRODUCTION VIA CARBONIZATION, GASIFICATION AND HYDRO-REFINING OF BY-PRODUCTS FROM TAR

	(A) in Rs	(B) in Rs	(C) in Rs
1. Phenols	18.00	7.70	7.20
2. Diesel Oil	84.00	36.10	33.60
3. Pitch	17.50	7.50	7.00
4. Sulphur	19.80	4.50	4.50
Total	139.30	55.80	52.30

ACTUAL COST OF PRODUCTION OF AMMONIA TAKING RECOVERY FROM BY-PRODUCTS

(A) in Rs	(B) in Rs	(C) in Rs	(D) in Rs
392.00 (-) 139.30 =252.70	409.50 (-) 55.80 =353.70	404.25 (-) 52.30 =351.95	264.00

*In line with the Assam coal the carbonization and gasification of the carbonized mass and the production of ammonia has been considered for coals of other regions. While in calculation it has been considered the investment cost of the plant and machineries will remain the same. However, in actual practice due to higher input of coal in comparison to Assam coal has to be taken into account and that will necessarily involve bigger capacity carbonizer and gasifier for coal of other regions. The production cost of ammonia per ton will be still higher than as shown above for coals other than Assam coal. For the production of a ton of ammonia from coals of other regions we have considered only the higher cost of coal due to high ash and moisture content and the low by-products recovery. All the other terms of capital cost as well as recurring expenditures remained the same as per Assam coal as shown in the above table.

†From the above table it can be seen the production of ammonia per ton from Assam coal is considerably cheaper even if we add to it the cost of transportation (say Rs. 50 per ton). Ammonia produced by utilizing Assam coal is cheaper than the cost of Ammonia produced from natural gas by a margin of nearly Rs. 10 per ton.

‡The calculations have been made for the production of ammonia from natural gas as per the price prevailing now. If it is to be utilized for a period of 10 years in that case the fixed charges on capital will be as above. On the other hand, if the gas is to be utilized by the method of recompression and preservation then the cost of natural gas would necessarily be higher. That invariably will raise the cost of ammonia per ton still further.

News in Brief

Superphosphoric Acid (72 per cent P_2O_5) for Liquid Fertilizers

The use of liquid fertilizers is increasing day by day. More and more liquid-mixing plants are coming up in U.S. farm belt. To meet the growing demand high analysis fertilizers is the need of the hour. Gulf Design Corp., Fla., has developed a process to produce more acceptable grade of superphosphoric acid (72 per cent P_2O_5) for liquid fertilizers by combining two existing methods of making super acid. The process yields a product 80 per cent less viscous than the "molasses". Fertilizer blenders can handle the improved acid more easily and ammoniate it to higher analysis liquid fertilizer.

The process consists of concentrating wet-process phosphoric acid (30 to 40 per cent P_2O_5) and heat for evaporation is provided by burning the elemental phosphorus. At the same time, gaseous P_2O_5 produced by burning elemental phosphorus is hydrated by feed acid to make up the final product. The resulting super acid is nothing but a blend of concentrated wet-process acid and thermal acid from the burning of elemental phosphorus. The contribution of the purer thermal acid accounts for the improved physical properties of the super acid—80 per cent reduction in viscosity and improved sequestering action to hold impurities in solution and inhibit their settling out.

In Gulf Design's process, the extent that thermal acid substitutes for wet-process acid is determined by the amount of elemental phosphorus burnt to evaporate water from the wet process acid. Most practically, produces would feed in 54 per cent P_2O_5 rather than 30 per cent P_2O_5 acid.

[C & EN, Dec. 11, (1967), 62]

Fertilizer From Household Waste

Ever expanding industries in the twentieth century are posing the problem of constant supply of raw materials, which day by day are getting exhausted. To run the industries one has to switch over to

alternative feedstocks. Discovering new raw materials or exploring the possibility of using available wastes is a continuous process and that is going on. Besides industrial wastes, various house hold refuses are also finding place as a feedstock in industry e.g. cardboard industry in India uses scrap papers and ragged clothes.

But putting to use almost all household waste including discarded chairs and even refrigerators also is something novel. This venture is made possible by a plant designed by a Wolverhampton firm, Lawdon Manufacturing Co. (Birmingham) Ltd. The plant accepts almost all household wastes to produce a product which is proposed to be christened as 'Orgin'.

Though technical details are not available, it is stated, that the product is fibrous and usable as a base for fertilizer and will be made in three grades. The unfortified material for use as soil conditioner, a Chemically Supplemented form (to be called sweet soil) for gradeners and a more heavily chemically supplemented form for commercial cropping use.

A £ 350,000 plant is estimated to produce over 300 tons of fertilizer a week from the wastes of a 100,000 population.

Operation of the plant, it is reported, on pilot-scale is not practicable and therefore the first plant will jump at once to full scale production.

[Fertilizer and Feeding-stuffs J., Jan. 17, (1968) 41]

A waste disposal system for one-family based on biological decomposition and fully independent of the water and sewer network has been developed by Rikard Lindsfrom of Tyrseo near Stockholm (Sweden). The final product of system is salts and humus which can be used as fertilizers.

The system consists of a garbage chute from the kitchen and a toilet which requires no flushing, both of which are connected via vertical pipes to a specially designed decomposition chamber made of

a reinforced impermeable plastics material situated in the cellar or partially buried outside. The waste material gathers at the top of this chamber where it decomposes biologically. During the decomposition process water vapour and carbon dioxide are formed and allowed to escape via an exhaust duct, the waste matter is reduced considerably in volume as it moves slowly towards the lower part of the container, where the final products accumulate in the form of salts and humus. A house hold of five to six persons produces a few buckets of fertilizer a year.

The system is suitable for camping or bathing sites, temporary labour camps, military training stations, agricultural establishments etc. The system is claimed to be simple to install, odour free, and there is said to be absolutely no danger of contamination of the surrounding soil.

[Science J., Feb. (1968), 21]

Phosphate Without Sulphuric Acid

Chemical Construction Corpr. of New York have developed a new nitrophosphate process without use of sulphuric or phosphoric acid. The process is characterized by no need for low temperature crystallization of calcium nitrate and is applicable to a wide variety of natural phosphate rock. It is one of the most economical among the processes for production of water-soluble phosphate fertilizer based on phosphate rock. It yields two fertilizers—ammonium nitrate and a nitrophosphate.

[Chem. Age., 97 (2525) (1967), 14]

Investment in Fertilizers

To keep pace with the expected populations growth, agriculture in Asia, Africa and Latin America will need 40 million tons of plant nutrient by 1985 compared to 6 million used in 1966. The production of this additional fertilizer will require \$ 17,000 million/year capital investment for the next 17 years just in fertilizer plants to supply the above continents. This

was quoted (from a recent report of the Presidents Scientific Advisory Committee) by Dr. Raymond Ewell of New York State University at a recent meeting. The PSAC report also stated that 400,000 tons of pesticides are needed in the above continents in 1985 compared with 120,000 tons used in 1966.

[*Chem. Age.*, 97 (2523) (1967, 10)]

Slow-Acting Fertilizers

Condensates which are useful as slow acting fertilizers with 26-35 per cent N are produced by reacting urea with a furfural/formaldehyde mixture in aqueous solution at a temperature between 20° and 35°C. Aqueous sulphuric acid is the catalyst. The molar ratio between the urea and the sum of furfural and formaldehyde may vary between 1.6 and 1.15. For each mole furfural, between 6 and 0.2 mole formaldehyde is used.

Between 1×10^{-4} and 2×10^{-3} mole sulphuric acid is used per mole urea. The water: urea ratio has such a value that a 55-56 per cent aqueous solution is formed.

[*ECN* 13 (315) (1968), 48]

Exchange Resin for Ammonia Recovery

Hydrocarbon/Continental Products Odesa, Texmaco, has developed a cation-exchange resin for recovering 80 per cent of ammonia from fertilizer plant waste streams. In an ammonium nitrate and nitric acid plant, the system could recover ammonium nitrate solution using nitric acid as regenerant.

[*Res. & Indus.* 12 (1967), 279]

Fertilizers on Grass—Planned Use of Nitrogen

On growing grass, Dr. John S. Brockman, Senior Grassland Officer at North Wyke Experimental Station said that the size and timing of Nitrogen dressings could become critical if sustained high output was required from grass. Nitrogen should be applied for every growth period, the size of the dressing being related to the number of days the sward is to be allowed to grow. These recommendations were based, he said, on three principles governing the heavy use of nitrogen which has emerged from work at North Wyke.

(1) Grass takes up nitrogen from a fertilizer dressing far in advance of growth response. Though the uptake of nitrogen begins soon after it is applied, the growth rate does not increase appreciably until 15 to 20 days after application.

(2) The correct size of nitrogen dressing depends on the length of time the swards will be allowed to grow. In general a sward's needs can be met by about 2 units of nitrogen per acre per day.

(3) Frequent small dressings give higher yields than infrequent large dressings. If a heavy nitrogen dressing is applied and the grass defoliated after a short period, full use of nitrogen will not be made. However, the grass will have taken up most of the nitrogen and therefore will not be available for subsequent growth.

[*Fertilizer and Feeding Stuff J.*, 64 (24) (1967), 844]

Ammonia Prevents Smut Formation

Ammonia prevents smut formation in oil-burning furnaces and cuts corrosion by 10 per cent, when it is mixed with combustion air. Smut forms when partially burned fuel coalesces in the presence of sulphuric acid, which exists where sulphur bearing fuels are burned. As little as 1 per cent ammonia dispersed in the combustion air is sufficient to neutralize the acid, thereby preventing particle coalescence and incidentally removing a corrosive agent. To prevent formation of sticky ammonium bisulphate which could create a worse problem than the original one, the air-ammonia mixture must be preheated to about 100°C.

[*Chem. Engng.*, Aug. 14. (1967), 87]

Sale of Fertilizers in India

Till the 30th September, 1966 the Central Fertilizer Pool used to take over the entire production of nitrogenous fertilizers in the country. With effect from 1st October, 1966, The Fertilizer Corporation of India Limited was authorised to sell 30 per cent of the production of fertilizers directly. From 1st October 1967, this was raised to 50 per cent and from 1st October 1968 the entire production of fertilizers can be sold directly by the Corporation subject to the condition that the Government of India will have the right to procure up to 30 per cent of the production at a negotiated price.

At present The Fertilizer Corporation of India has three production units at Sindri, Nangal and Trombay. Almost all the fertilizer produced at Nangal is earmarked for direct sale. It has been and is being distributed through Punjab and Haryana State Co-operative Supply and Marketing Federations. A small 14,000 tonnes has been kept aside for distribution in U.P. and other states. As regards Sindri, distribution

of the direct sale quota to the extent possible is arranged through Bihar State Co-operative Marketing Union. Some sales have also been effected to co-operatives in U.P. and private parties. In respect of fertilizers produced by the Trombay unit, the distribution of direct quota is being arranged partly by the Corporation's own marketing organization and agents, and partly by co-operatives.

Up to two months' credit is allowed to co-operative societies on interest. But no interest is charged if payment is made within a month.

(Lok Sabha: February 19, 1968)

[*Oil Commentary*, 5 (11) (1961), 13]

Processed Fertilizer From Leaves

Dr. Sanjiva Rao of the Indian Institute of Science, Bangalore, has developed a processed fertilizer from green leaves to act as stimulant for plant growth. Called 'Leadnip', it has the same properties of stimulation for plant growth as 'humophos', a fertilizer developed by Russians.

[*Res. & Indus.*, 12 (1967), 274]

Nitrogen for Inflation of Car Tyres

According to research, principal reason for deterioration of tyres is internal oxidation caused by the 20 per cent of oxygen in air, which affects both the tyre rubber and fabric. Tyre makers normally treat tyre rubber compounds with anti-oxidants, but this is reported to be only partially successful in combating oxidation.

Testing carried out by one company of U.S.A. indicates that oxygen free gases substantially improved tyre mileages of both cars and Trucks. Inflation with nitrogen will tend to increase the life of the tyre. Cost of inflation of new tyres with nitrogen is suggested at 50cent per tyre.

[*Nitrogen*, No. 50, (1967), 38]

New Route to Ammonia Suggested by Russian Workers

A new route to ammonia production is reported to have been worked out in Russia by workers at the U.S.S.R. Academy of Sciences. The new process is based upon a homogeneous molecular catalyst for nitrogen fixation and should permit reduction in the final stage pressures of current processes and hence make possible a considerable reduction in the capital cost of such plants.

The Russian investigators report the conversion of gaseous nitrogen into ammo-

nia at room temperatures and at atmospheric pressures with dicyclo-pentadienyltitanium dichloride in the presence of ethylmagnesium halide.

In the U.S., the University of Michigan has confirmed and refined this research and reports that a titanium hydride complex, a dimer of dicyclopentadienyltitanium hydride, having a reduction equivalent of six is formed, precisely the number required to handle the nitrogen triple bond. The catalyst is recovered readily after the ammonia is removed from the solution by acid hydrolysis.

Currently the problem in ammonia synthesis is the high pressure required in the final stage, and if it could be reduced and the compressors removed, the capital cost of such a plant could be almost halved. Other problems are that if the steam from the natural gas reformers is not used as a source of power to drive these machines it will have to be utilized elsewhere to maintain the economics of the cracking process. Also to be considered is the cost of iridium or titanium.

[*ibid*]

Fertilizer from Industrial Waste

A new biomineral fertilizer has been developed under a joint project by the Ukrainian Academy of Sciences and the Dnepropetrovsk Agricultural Institute. Industrial waste materials, such as brown coal dust, peat, cement dust and gasworks

effluent, are treated with bacteria, which set off biochemical processes releasing plant nutrients over a long period. The fertilizer has a nutrient content of about 20 per cent nitrogen, phosphorus and potassium, but their relative proportions can be altered by changing the mixture of wastes employed. Nitrogen content can be increased by using a larger proportion of ammoniacal waste from gas works, which also neutralizes the acidity of some of the other wastes used. Slags will provide more phosphorus, and cement dust more potassium. The bacteria used are cultivated specially and propagate at only a little above room temperature.

The process requires no complex equipment, and utilizing waste materials, the product is extremely cheap. It is a loose, powder-like substance and therefore easily transportable, and has been shown to be more efficient than a double or even triple dosage of natural manure. One application every five years is sufficient for good, stable harvests, and it seems that the fertilizer is more effective in the second year after application than in the first. Three pilot plants have been operating since 1964 in the Ukraine, in the Kiev, Zhitomir and Chernigov regions, and it is claimed that now the test period has been completed, these three plants will have an annual output of 400,000 tons of fertilizer.

[*ibid* 40]

Shortage of Naphtha

A detailed study made by the Indian Institute of Petroleum (CSIR) has revealed a possible shortage of nearly 2 m. tonnes of naphtha by 1975-76. The study has proposed that the refineries may, wherever possible, process lighter crudes so as to increase the yield of naphtha. The production of naphtha can also be increased by adjusting the pattern of distillation of crude oil. The use of secondary processing such as hydro-cracking in selected plant has also been recommended.

The comparative economics of ammonia production will depend on the price at which naphtha will be available at home and by import. Naphtha prices abroad have lately hardened and there has been increasing pressure on its availability in international markets.

(Source: Rajya Sabha 13.2.1968)

[*Oil Commentary*, 5 (10) (1968), 14]

Desalination of Waste Water from Ammonium Sulphate

A new process for the desalination of waste water from the production of ammonium sulphate has been developed at the Friedrich Schiller University, Jena (E. Germany). Extraction of upto 3,000 tons of ammonium sulphate will be possible per plant annually.

[*ibid*]

STATISTICS

TABLE 1—COMMERCIAL FERTILIZERS: PRODUCTION AND CONSUMPTION

Country	Production						Consumption					
	July-June						July-June					
	1965-66			1966-67			1965-66			1966-67		
	Nitrogen (N)	Phosphate (P ₂ O ₅)	Potash (K ₂ O)	Nitrogen (N)	Phosphate (P ₂ O ₅)	Potash (K ₂ O)	Nitrogen (N)	Phosphate (P ₂ O ₅)	Potash (K ₂ O)	Nitrogen (N)	Phosphate (P ₂ O ₅)	Potash (K ₂ O)
United Kingdom	665.9	419.9	—	732.1	403.1	—	689.7	421.8	436.3	760.4	439.1	455.7
France	1,066.0	1 217.6	1 877.1	1 223.5	1 330.0	1 836.6	870.6	1 258.8	969.8	990.0	1 363.8	1 024.3
Italy	904.9	512.3	173.3	950.1	516.1	175.1	461.8	452.6	167.6	475.3	462.8	173.2
Germany Eastern	348.4	231.8	1 926.0	344.1	253.9	2 006.0	421.4	302.5	588.4	*450.0	*330.0	*630.0
Federal Republic of Germany	1 418.9	856.8	2 334.8	1 501.3	860.7	2 119.7	873.8	819.1	1 190.3	888.6	791.8	1 076.8
U.S.S.R.	2 712.0	1 599.0	2 368.0	*3 100.0	*1 710.0	*2 650.0	2 282.0	1 504.0	1 821.0	2 656.0	1 664.0	1 902.0
U.S.A.	5 081.0	4 260.0	2 592.0	5 535.0	4 651.0	2 811.0	4 831.9	3 393.5	2 922.2	5 487.1	3 855.8	3 287.9
Pakistan	93.4	1.2	—	*93.1	*0.7	—	132.7	11.2	*5.0	*170.0	*30.5	*14.0
Israel	24.6	12.9	315.0	24.8	14.2	297.5	23.9	12.0	4.4	24.7	13.0	4.6
Japan	1 615.0	588.0	—	*1 801.2	*655.2	—	775.0	546.0	607.0	*850.0	*630.0	*640.0
India	232.0	*118.8	—	*309.0	*150.7	—	540.8	134.3	*89.6	*830.2	*274.0	*133.6
China Mainland*	*500.0	*350.0	*100.0	*800.0	*360.0	*100.0	*1 050.0	*350.0	*100.0	*1 850.0	*365.0	*105.0
U.A.R.	157.3	44.7	—	*165.0	*50.0	—	285.2	54.7	*1.0	*250.0	*55.0	*1.0
World Total	19 800	15 400	3 900	22 200	16 500	14 500	18 700	14 600	12 300	21 800	15 800	13 100

*Unofficial figure

[Monthly Bulletin of Agricultural Economics and Statistics, FAO 17 (2), 1968, p. 26]

TABLE 2—WORLD PHOSPHATE ROCK EXPORTS

('000 tonnes Product)

	1965	1966
Morocco	9,553	9,202
Tunisia	2,308	2,395
Algeria	55	38
Togo	982	1,111
Egypt	373	430*
Senegal	956	1,188
Israel	308	432
Jordan	605	755
U.S.A.	6,759	8,364
Nauru, Ocean, Christmas Islands	2,688	3,474
Makatea	330	188
Curacao	110	147
Mexico	31	35*
Total Free World	25,058	27,759
U.S.S.R.	3,575	
North Vietnam	450*	4,500*
Grand Total	29,083	32,259

*Estimate

[Phosphorus and Potassium, No. 27, Jan/Feb, 1967, 1]

TABLE 3—IMPORTS OF POTASSIC FERTILIZERS DURING
1967-68
(April-March)

Material and source of import	April to June 1967	July to Sept. 1967	Octr. to Dec. 1967	Jan. to March 1968	Total April 1967 to March 1968
<i>Muriate of Potash (60% K₂O)</i>					
Canada	10736	60001	14600	—	85337
France	—	—	—	27528	27528
Germany East	28700	22435	36126	39384	126645
Hungary	15450	—	—	—	15450
P.F.L.*	750	20550	47200	8000	76500
U.S.A.	—	—	30506	34717	65223
U.S.S.R.	13946	—	—	3573	17519
Total	69582	102986	128432	113202	414202
<i>Muriate of Potash (50% K₂O)</i>					
Germany East	8382	2999	4500	6619	22500
<i>Sulphate of Potash (50% K₂O)</i>					
Germany West	5000	—	—	—	5000
<i>N.P.K. Mixture (14-14-14)</i>					
U.S.A.	19894	16960	39942	—	76796
Equivalent K ₂ O	51225	65666	84901	71231	273023

*The imports arranged through Potash Fertilisers Ltd., London, from various countries are not available.

Source: (i) Indian Potash Supply Agency Ltd., Madras.
(ii) Ministry of Food and Agriculture, New Delhi.
[FAI Information Serv. 9 (9) (1968), 8]

TABLE 4—SUPPLY POSITION OF ROCKPHOSPHATE AND SULPHUR DURING 1967 (Jan/Dec.)

I. Rockphosphate

(Long tons)

Country of origin (1)	Contracted quantity (2)	Supplies effected (3)	Balance expected (4) =(2)-(3)	Spill over from 1966 (5)
Tunisia	150,000	—	150,000	47,238
Jordan	250,000	347,125	52,875	—
	+150,000			
Togo	30,000	32,781	—	—
Florida	10,000	10,000	—	—
U.A.R.	150,000	26,414	123,586	10,300
Algeria	—	—	—	62,182*
Total	740,000	416,320	326,461	119,720

Total quantity received during the year = 416,320 + 119,720
= 536,040

*This includes 9,957 tonnes of rock from Senegal supplied in lieu of an equal balance quantity of Algerian rockphosphate.

II. Sulphur

Country of origin (1)	Contracted quantity (2)	Supplies effected (3)	Balance expected (4)=(2)-(3)
Taxes Gulf	100,000	85,943	14,057
Free Port	105,000	82,958	22,042
Through S.T.C.	230,000*	149,402**	80,598
Others & AUL	350,000*	350,000**	—
	785,000	668,303	116,697

*Estimate.

**Includes estimate for December 1967.

[Fertilizer News, 13 (4) (1968), 42]

TABLE 5—EXPORT OF NAPHTHA & FURNACE OIL FROM INDIA

Product Exported to:	1966		1967	
	Quantity ('000 tonnes)	Value (Rs. lakhs)	Quantity ('000 tonnes)	Value (Rs. lakhs)
<i>Naphtha</i>				
U.K.	169.23	164.61	302.84	328.20
Japan	17.34	13.43	207.24	249.37
Holland	55.45	41.21	55.64	58.27
South Korea	—	—	31.36	37.03
Singapore	16.36	20.15	16.73	21.08
New Zealand	123.63	127.36	—	—
U.S.A.	100.78	90.74	—	—
Bahrein	15.41	13.75	—	—
Total	498.20	471.25	613.81	693.95
<i>Furnace oil</i>				
Thailand	—	—	45.74	26.84
Ceylon	—	—	15.50	14.08
Total	—	—	61.24	40.92
Grand Total	498.20	471.25	675.05	734.87

Source: Oil Statistics, Vol. V. No. 4, October-December 1967.
[FAI Information Serv. 9 (8) (1968),]

TABLE 6—POOL ISSUE PRICES OF NITROGENOUS FERTILIZERS, METRIC TONNE

[Effective from April 1, 1968]

1. (a) Ammonium Sulphate 100 kg. packing	Rs. 447/-	per M.T.
(b) Ammonium Sulphate 50 kg. packing	Rs. 458/-	"
2. Urea	Rs. 780/-	"
3. Muriate of potash (60-62% K ₂ O)	Rs. 445/-	"
4. Calcium ammonium nitrate (20.5%)	Rs. 385/-	"
-do- (25%)	Rs. 455/-	"
-do- (26%)	Rs. 475/-	"
5. Ammonium Sulphate Nitrate	Rs. 515/-	"
6. Diammonium phosphate	Rs. 1000/-	"
7. Ammonium phosphate	Rs. 738/-	"
8. Ammonium chloride	Rs. 450/-	"

In the case of distributors of Plantations the prices in respect of items 1(a), 1(b) and 2 have been revised as Rs. 472, Rs. 483 and Rs. 820 with effect from April 1, 1968.

[FAI Information Serv. 9 (8) (1968), April 16]

TABLE 7—FUTURE FERTILIZER FACTORIES

Name of Project (1)	Investment (Rs. crores) (2)	Annual Capacity (In terms of Nitrogen) (3)	Name of party (4)	Name of foreign collaborator (5)	Salient features of foreign collaboration (6)
I. Public Sector					
Durgapur	43.4	152,000	Fertilizer Corporation of India	No foreign collaborator	The foreign exchange requirement is mostly covered by the Suppliers' Credit from Italy.
Cochin	45.6	152,000	Fertilizers & Chemicals Travancore Ltd.	-do-	-do-
FACT (IV Stage Expansion)	5.0	22,000	-do-	-do-	The foreign exchange requirement is covered by the Yen Credit.
Madras	54.6	190,000	Madras Fertilizers Ltd.	Amoco India, Incorporated of USA	The foreign exchange requirement has been arranged by the foreign collaborators partly through equity and partly through loans from Banks.
Barauni	35.1	152,000	Fertilizer Corporation of India	No foreign collaborator	The foreign exchange requirement is mostly covered by the Suppliers' Credit from Italy.
Namrup Expansion	29.50	152,000	-do-	-do-	-do-
Trombay Expansion	51.0	229,000	-do-	-do-	The foreign exchange requirement is expected to be arranged through US AID.
II. Private Sector					
Kota	27.0	130,000	Delhi Cloth & Gen. Mills Co. Ltd.	-do-	The foreign exchange requirement has been arranged through Suppliers' Credit from Japan.
Gujarat Expansion	22.3	120,000	Gujarat State Fertilizer Co. Ltd.	-do-	-do-
Kanpur	58.9	200,000	Indian Explosives Ltd.	M/s. I.C.I. (London) & International Finance Corporation	The foreign exchange requirement has been arranged mostly by ICI (London) and IFC, Washington. A small portion is also covered through Suppliers' Credit from Japan.
Goa	47.2	160,000	Birla Gwalior Pvt. Ltd.	M/s. Armour & Co. and International Finance Corporation	The foreign exchange required will be arranged by M/s. Armour & Co. and the IFC, Washington
Ghaziabad	36.0	160,000	Modi Spg. & Wvg. Co. Ltd.	Rohm & Hass of USA.	Foreign collaboration proposals yet to be finalised.
Mirzapur	46.0	160,000	Pilaini Investment Corpn.	Kaiser Group, USA.	-do-
Vizag Expansion	23.0	155,000	Coromandel Fertilizers Ltd.	International Mineral & Chemicals Corpn. & California Chemical Co.	This is expansion of the existing project. The foreign exchange requirement will be arranged by the foreign collaborators.
Mangalore	52.5	240,000	Malabar Chemicals & Fertilizers Ltd.	International Development & Investment Co. Ltd. Nassau.	Foreign collaboration proposals are to be finalised.
Dharamsi Morarji Chemical Co. Project in Maharashtra	23.0	90,000	Dharamsi Morarji Chemical Co.	Kuwait Chemicals & Fertilizer Co.	-do-

[OIL COMMENTARY, 5 (11) (1968), 14 & 15]

TABLE 8—REQUIREMENT AND PRODUCTION OF FERTILIZERS IN INDIA

	Total annual requirement (million tonnes)	Total annual production (million tonnes)	Annual shortfall (million tonnes)
Nitrogenous Fertilizers (In terms of N)			
1967-68	1.35 (Value Rs. 283.50 crores)	0.36 (Value Rs. 75.60 crores)	0.99
1968-69	1.70 (Value Rs. 357.0 crores)	0.65 (Value Rs. 136.50 crores)	1.05
1969-70	2.00 (Value Rs. 420.0 crores)	0.98 (Value Rs. 205.80 crores)	1.02
Phosphatic Fertilizers (In terms of P_2O_5)			
1967-68	0.50 (Value Rs. 120.0 crores)	0.20 (Value Rs. 48.0 crores)	0.30
1968-69	0.65 (Value Rs. 156.0 crores)	0.33 (Value Rs. 79.20 crores)	0.32
1969-70	0.80 (Value Rs. 192.00 crores)	0.38 (Value Rs. 91.20 crores)	0.42
Potassic Fertilizers (In terms of K_2O)			
1967-68	0.30 (Value Rs. 24.0 crores)	Nil	0.30
1968-69	0.45 (Value Rs. 36.0 crores)	Nil	0.45
1969-70	0.55 (Value Rs. 44.0 crores)	Nil	0.55

(Lok Sabha: February 19, 1968)

[OIL COMMENTARY 5 (11) (1968), 16]

TABLE 9—PRODUCTION OF FERTILIZERS & CHEMICALS AND
CONSUMPTION OF SOME RAW MATERIALS IN FCI'S SINDRI
FACTORYDuring 1967-68
(April 1967 to March 1968)

Ammonium Sulphate	241,300 tonnes
Urea	16164.35 „
Double Salt	60384 „
Coal Tar	11146.50 „
Motor Benzol	560426 l. gross
Pure Benzol	1114917 l. „
Refined Toluol	196213 „
Light Solvent Naphtha	114096 „
Wash Oil	285862 „
Road Tar	179.1 „
Chalk	371167 tonnes
<i>Raw Materials</i>	
Coking Coal	309402.15 „
Gypsum	533326.0 „

[Annual Statistics, 1967-68, (Prod. Stat. Sec., FCI Ltd.,
Sindri Unit, 1968)]